Synthesis, Structural Analysis and Self-Assembly Study of Supramolecular Janus Dendrimers

BY

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Dedicated to my father and mother

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF SCHEMES

LIST OF TABLES

LIST OF ABBREVIATIONS

CDMT	:	2-Chloro-4,6-dimethoxy-1,3,5-triazine
NMM	:	N-Methylmorpholine
DCC	:	N,N'-Dicyclohexylcarbodiimide
DPTS	:	1,4-Dimethylpyridinium *p*-toluenesulfonate
TOPM	:	Thermal Optical Polarized Microscopy
DSC	:	Differential Scanning Calorimetry
TGA	:	Thermal Gravimetric Analysis
LC	:	Liquid Crystalline
NMR	:	Nuclear Magnetic Resonance
TMS	:	Tetramethylsilane
TLC	:	Thin Layer Chromatography
THF	:	Tetrahydrofuran
DCM	:	Dichloromethane
EO	:	Ethylene Oxide
Me	:	Methyl
Bu	:	Butyl

ABSTRACT

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Wedge-shape amphiphilic dendrons containing long hydrophobic chains on the periphery and relatively small hydrophilic groups at the apex positions of the dendrons can self-assemble into supramolecular columns or spheres that can self-organize into various two-dimensional columnar as well as three–dimensional cubic periodic arrays. Twin-tapered dendrimers, containing two identical dendrons attached to each other, can also self-assemble into supramolecular columns generated by an orthogonal *H*-bonded stack of supramolecular columns that self-organize into periodically ordered columnar assemblies or co-assemble into more complex superlattices. Janus-dendrimers represent a new class of supramolecular amphiphiles containing two structurally different dendritic building blocks attached to each other by chemical bonds. These supramolecular Janus dendrimers can exhibit thermotopic liquid crystalline (LC) properties in their self-assembled state.

In this work, new libraries of twin and Janus dendrimers have been synthesized. Characterization and structural analysis of these new dendrimers has been performed. The self-assembly mechanism and the LC behavior of these supramolecular dendrimers has been studied.

ملخص الرسالة

الاسم الكامل: أحمد صلاح عبد الله ندا

عنوان الرسالة: تحضير و التحليل البنائي و دراسة التجمع الذاتي للدندريمرات فوق الجزيئية مزدوجة الوجه

التخصص: الكيمياء

تاريخ الدرجة العلمية: مايو 2018

يمكن للدندرونات ذو الشكل الوتدي التي تحتوي على سلاسل طويلة كارهة للماء على السطح الخارجي ومجموعات صغيرة نسبياً محبة للماء في موقع الرأس أن تتجمع ذاتيًا في شكل أعمدة أو كرات فوق جزيئية و التي بدورها يمكنها أن تنتظم ذاتيًا في أشكال عمودية متنوعة ثنائية الأبعاد بالإضافة إلى صفائف دورية مكعبة ثلاثية الأبعاد. يمكن أيضاً للدنريمرات التوأم التي تحتوي على شقين متماثلين متصلين ببعضهما البعض، أن تتجمع في أعمدة فوق جزيئية و التي تنتظم ذاتيًا في مجموعات عمودية مرتبة بشكل دوري أو تشارك في التجمع في أعمدة فائقة أكثر تعقيدًا. تمثل الدندريمرات مزدوجة الوجه نوع جديد من اللفائف فوق جزيئية التي تحتوي على كتل بناء شجيرية مختلفة البنية مرتبطة ببعضها البعض بواسطة الروابط الكيميائية. يمكن لهذه الدندريمرات فوق جزيئية مزدوجة الوجه أن تحمل خصائص السائل البلوري في حالة تجمعها الذاتي.

في هذا العمل ، تم تحضير مجموعة جديدة من الدندريمرات التوأم و مزدوجة الوجه. تم إجراء التوصيف والتحليل البنائي لهذه الدندريمرات الجديدة. وقد تم دراسة آلية التجمع الذاتي وسلوك السائل البلوري لهذه الدندريمرات فوق جزيئية .

CHAPTER 1

INTRODUCTION

Dendrimers [1,2] are new class of polymeric materials. They are perfect monodisperse macromolecules with a regular and well-defined three-dimensional architecture that are currently explored at the interface between chemistry, biology, physics, medicine, and nanoscience [3-6]. The word dendrimer comes from Greek *dendron* meaning tree and *meros* meaning part. Dendrimers were first discovered as "cascade molecules" in the late 1970s by Vogtle et al. [7]. After the seminal work by Tomalia et al. [8] and Newkome et al. [9] in the mid-1980s, dendrimers now become a rapidly growing area of science and technology [1,2]. The synthetic capability of dendrimers in a wide range of size (i.e., generations) combined with their unique structure makes them versatile building blocks for a wide range of application, such as, catalysis [10], drug delivery [11], light-emitting diodes (OLED) [12], sensors [13], etc. Recently there is a great deal of interest of using dendrimers in nanoscience [14].

1.1 Structure of dendrimers

Typically, a dendrimer is consisted of a core or focal point, multilayers of branching units and a layer of end groups on the periphery. The number of branching layers derived from

the core to the surface is called the dendrimer generation. The primary structural unit or a fragment of a supramolecular dendrimer is known as dendron (Figure 1).

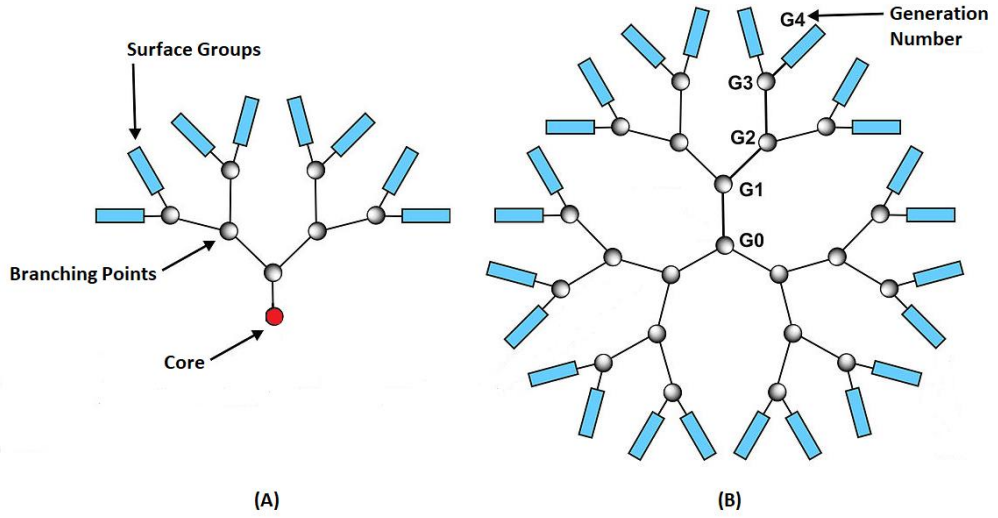


Figure 1 Schematic representation of dendron (A) and dendrimer (B).

1.2 Construction of dendrimers

Over the past three decades, two major synthetic strategies for dendrimer synthesis have emerged: the divergent and convergent approaches. In both methods, the synthesis requires a stepwise process, which is the reason for the monodisperse composition.

1.2.1 The divergent approach

In the *divergent* approach [8], dendrimers are built from the central core out to the periphery. In each reaction step a fixed number of reactive groups on the periphery of the dendron react with monomer units to form a new layer of generation to the dendron (Figure 2).

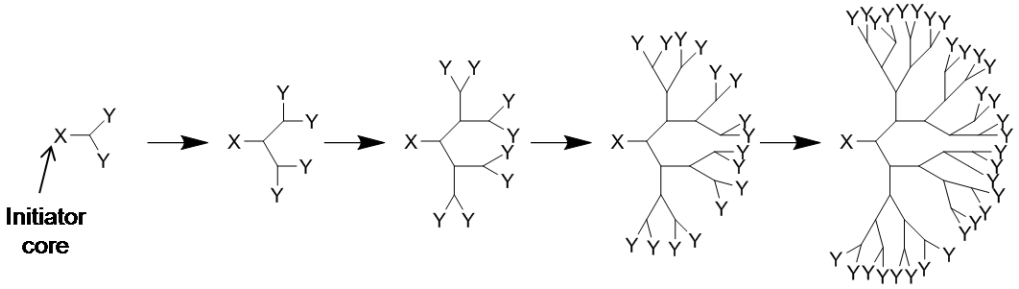


Figure 2 Schematic representation of the divergent approach.

At the start, an activated core is coupled to several branching units with 'inert' surface to form a dendrimer of the next generation. The 'inert' surface is then activated and further coupled to another layer of branching units to form a dendrimer of the next generation. By repeating this iterative procedure, dendrimers of higher generation can be prepared.

The divergent approach is considered a rapid method that allows one to prepare dendrimers of high generations in a highly efficient manner. In fact, most of the commercially available dendrimers are prepared using divergent synthesis under optimal conditions.

1.2.2 The convergent approach

In the *convergent* approach [15], dendrimers are constructed from the periphery toward the central core. Thus, the initial reaction sites ultimately stay on the periphery of the dendrimer, while the reactions take place on the reactive core (Figure 3).

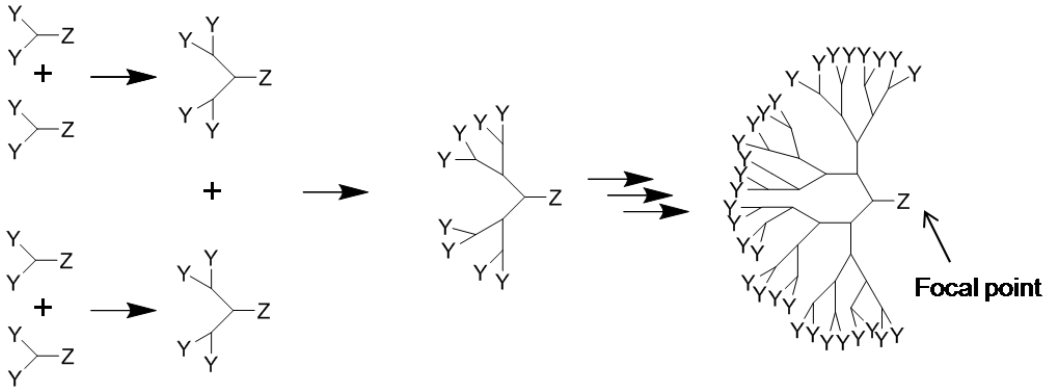


Figure 3 Schematic representation of the convergent approach.

Several peripheral segments bearing an active focal point functionality are coupled complementary to a branching unit made up of multiple active sites and an 'inert' focal point, yielding a dendron of a higher generation. The 'inert' functionality is then activated and converted to intermediate, which allows further iterative coupling reactions.

In contrast to the divergent approach, the convergent synthesis has a limited number of reactions during generation growth, which guarantees that the coupling and activation reactions can proceed to completion without generation of defective species. In addition, purification of target products becomes feasible due to the large difference in properties

of the product and starting materials. These features allow dendrimers to be synthesized in a well-controlled manner.

However, the fraction of the reactive focal point functionality gradually decreases, and steric inhibition increases at the focal point of high generation compounds. In order to ensure complete anchorage of dendrons during the synthesis of high generation dendrons, large amount of starting materials is needed, and this again leads to purification problems. Nevertheless, convergent synthesis allows better control and has higher versatility. As a result, functional dendrimers are mostly prepared by the convergent synthesis strategy.

1.3 Amphiphilic dendrons

Most dendritic structure relies on architectural motifs based on polypropylene mine (PPI) [16], polyamidation (PAMAM) [17] and Fréchet-type [18] dendrimers that do not self-organize into lattices. In contrast, Percec's amphiphilic dendrons (Figure 4) which are wedge-shape dendrons containing long hydrophobic chains on the periphery and relatively small hydrophilic groups at the apex positions of the dendrons, have the capability to self-organize into well-defined lattices [19,20].

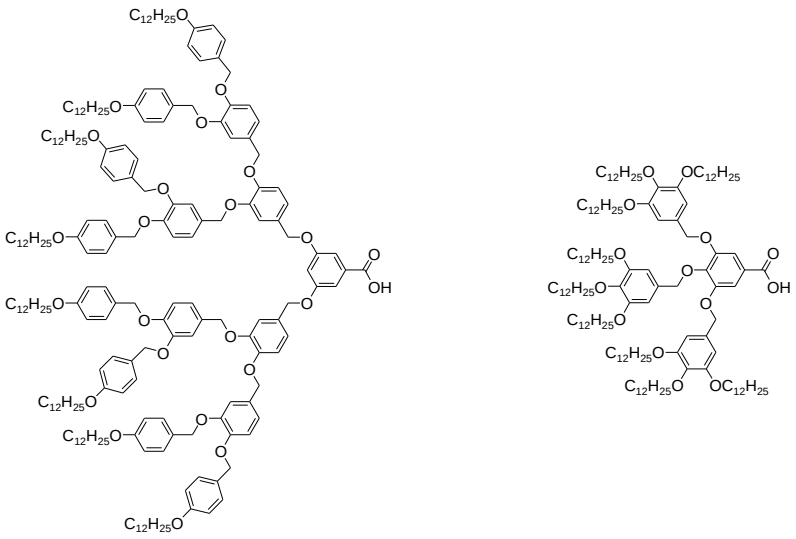
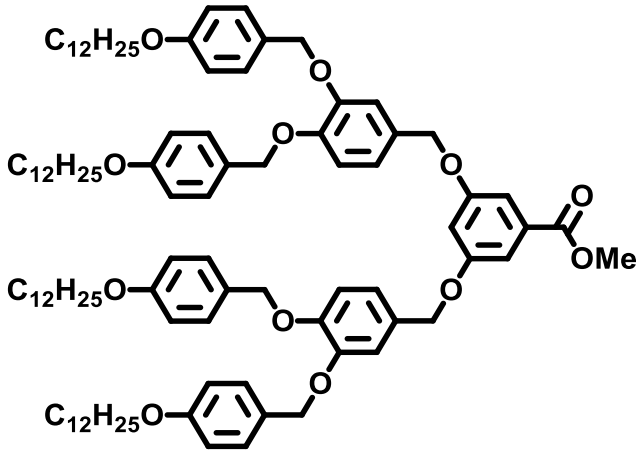


Figure 4 Examples of Percec's amphiphilic dendrons.

1.3.1 Nomenclature of Percec-type amphiphilic dendrons

A specific nomenclature has been developed to describe Percec-type amphiphilic dendrons [21]. For example, examine (4-3,4-3,5)12G2-CO_2Me (Figure 5). The numbers inside the parentheses denote the sequence of AB_n branched building blocks from the periphery to the apex. The number indicates from which position of the phenyl unit the B branches emanate. A descriptor such as Bp or Pr indicates a nonbenzyl branching unit such as biphenyl methyl or phenylpropyl, respectively. The number or descriptor following the parentheses indicates the number of carbons in the aliphatic tail, or alternative periphery unit. Following the periphery descriptor is the generation number. In this case, as there is an AB spacer unit followed by two AB_2 branching units, this molecule is a G2 dendron. The final descriptor is the apex functionality, which in this case is a methyl ester. In earlier reports, (3,4,5)*n*G1, (3,4)*n*G1, and even (4-3,4,5)12G1-CO_2Me were not referred to as dendrons. Later, after higher generations of dendrons and

dendrimers generated from these building blocks were reported by Percec's laboratory, these "minidendrons" were simply referred to as G1 dendrons.



(4-3,4-3,5)12G2-CO_2Me

Figure 5 Nomenclature of Percec-type amphiphilic dendrons.

1.3.2 Self-assembly of amphiphilic dendrons

Dendritic building blocks encoded with information that defines their three-dimensional shape and how they associate with each other are referred to as self-assembling dendron [22]. Amphiphilic dendrons adopting the shape of a disc or a fragment of a disc can self-assemble into supramolecular columns that self-organize into various two-dimensional columnar periodic assemblies [19]. Amphiphilic dendrons that adopt the shape of a sphere fragment can self-assemble into spherical supramolecular dendrimers, which self-

organize into various three-dimensional cubic periodic [23] and quasi-periodic [24] arrays (Figure 6).

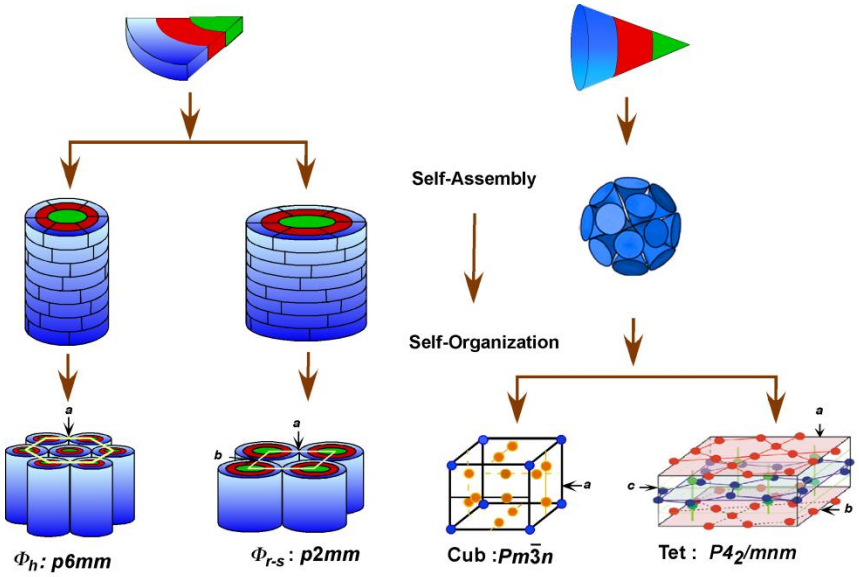


Figure 6 Schematic representations of the 2D and 3D periodic arrays self-organized from dendritic building blocks.

1.4 Twin and Janus dendrimers

Twin-tapered dendrimers (a dendrimer containing two identical dendrons attached to each other by a chemical bond) can also self-assemble into supramolecular columns generated by an orthogonal *H*-bonded stack of the dendrimer. These supramolecular columns self-organize into periodically ordered *p6mm* hexagonal assemblies or co-assemble into more complex hexagonal superlattices [25] (Figure 7A).

Janus-dendrimers are structurally similar to twin-dendrimers but contain two different structural motifs attached to each other by covalent bonds (Figure 7B). Linking two chemically distinct dendritic building blocks forms a Janus dendrimer, which breaks the roughly spherical symmetry that characterizes most dendrimers. Rational design of Janus dendrimers can incorporate fluorophobic, polar and nonpolar, hydrophilic and hydrophobic elements in the same molecule [26]. The self-assembly of Janus dendrimers can incorporate a large diversity in supramolecular architectures, like columnar, globular, and bilayered structures [27].

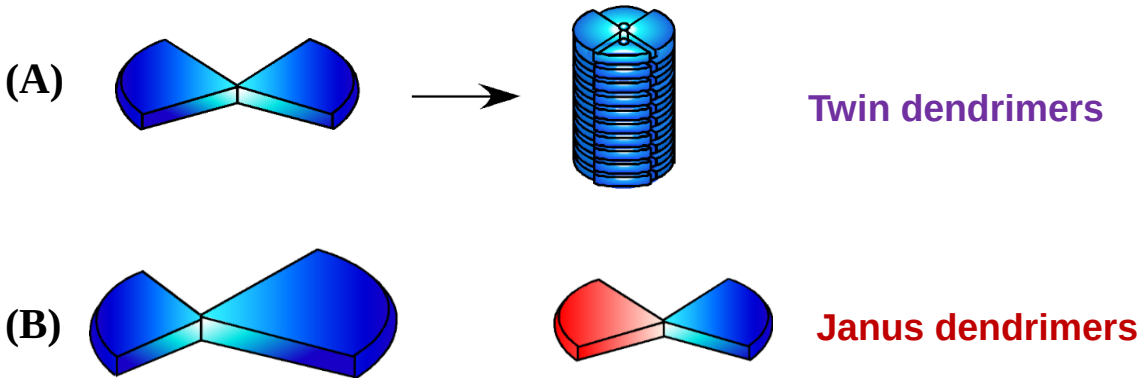


Figure 7 Twin and Janus dendrimers.

1.5 Applications of amphiphilic dendrons and supramolecular dendrimers derived from them

The supramolecular dendrimers and dendritic macromolecules, generated from the self-assembly of amphiphilic building blocks, have the shape perfection to allow self-organization into a large variety of two-dimensional columnar and three-dimensional cubic periodic and quasi-periodic arrays (Figure 6). This design strategy was exploited to create synthetic protein mimics [28,29], complex electronic materials [30], dendritic capsules [31], ionic liquids [32] and nanomechanical functional dendronized polymers [33,34]. Self-assembling amphiphilic dendrons are also used to functionalize rigid triphenylene and cyclotriveratrylene central cores to create a novel "crown-like" supramolecular assembly that self-organizes into pyramidal columns and hollow spheres [35,36].

Figure 8 represents a top view of amphiphilic dendritic dipeptide that self-assemble in solution and in bulk into hollow supramolecular columns that can transport protons acting as a protein mimic [29].

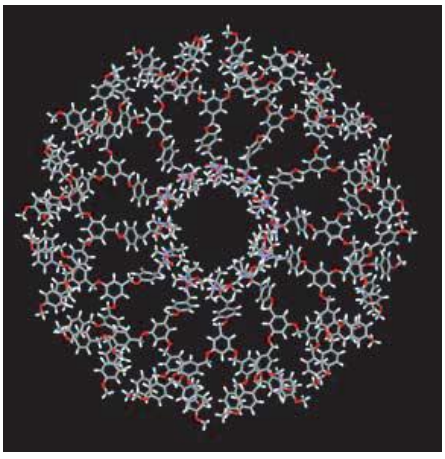


Figure 8 Amphiphilic dendritic dipeptide used as a protein mimic [29].

Figure 9 represents a conical dendron that self-assemble into hollow spherical supramolecular dendrimer. Functionalization of the apex of the conical dendron with specific functionalities allows the encapsulation of certain small molecules in the center of the hollow sphere [31].

Figure 9 Use of amphiphilic dendrons for encapsulation of small molecules [31].

The self-assembling dendritic approach was also exploited to design a novel architectural concept of liquid crystalline superlattices [25]. This concept is based on twin-dendritic benzamides and polymers containing twin-dendritic benzamide side groups. In twin-dendrimers, two identical dendrons are attached to each other by a chemical bond, such as amide linkage. It has been demonstrated that, twin-dendritic benzamide based on the two AB_3 dendritic building blocks can self-assemble into supramolecular cylinders that self-organize in a hexagonal (Φ_h) lattice [37]. The same twin-tapered dendritic molecules attached to a polymethacrylate backbone self-assemble into an imperfect cylindrical

bundle of supramolecular dendrimer that forms a novel giant vesicular super cylinder that self-organizes in a nematic (N_c) phase with short-range hexagonal order.

Janus-dendritic benzamide (that is, a benzamide containing two different dendrons) was first synthesized by the selective attachment of nonfluorinated (hydrogenate aliphatic) aliphatic chains on one dendron and semifluorinated aliphatic chains on the other dendron of the twin-tapered dendritic benzamides [27], The semifluorinated Janus-dendritic benzamides self-assemble into supramolecular bilayered pyramidal columns exhibiting more than double the diameter of the columns generated from non-fluorinated or semifluorinated twin-dendritic benzamides. Self-assembly of Janus Dendrimers were successfully utilized to create a novel class of compounds known as dendrimersomes, which serve as mimics to biological membranes [26]. These dendrimersomes are Janus dendrimers containing hydrophobic and hydrophilic segments in the structure (Figure 9) that can self-assemble in water to form bilayer vesicles with excellent stability and mechanical strength [26]. Recently, a library of self-assembling amphiphilic Janus dendrimers with two different monosaccharides and one type of disaccharide in their hydrophilic part of the dendrimer is reported [38]. Experimental evidences showed that these sugar-containing amphiphilic Janus glycodendrimers self-assemble into a diversity of hard and soft assemblies, including unilamellar spherical, polygonal, tubular vesicles, rod like micelles, and solid lamellae. These supramolecular assemblies are found to be stable over time in water and in buffer solution.

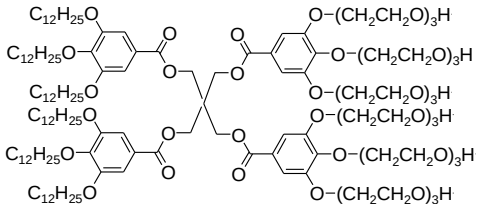


Figure 10 Representative example of Janus dendrimer acts as dendrimersome [26].

Synthesis, characterization and phase behavior of Janus-like supramolecular liquid crystals were reported by Saez and Goodby [39]. These compounds are based on a central scaffold made up of pentacrythritol and tris(hydroxymethyl)amino methane units linked together, where one of the units bears three cyanobiphenyl and the other chiral phenyl benzoate mesogenic moieties. These Janus micelles exhibit chiral nematic and chiral smectic phases. A pH-sensitive dual-targeting drug carrier based on Janus-like poly(amidoamine) dendrimers conjugated with transferrin on the exterior and tamoxifen in the interior of the dendrimers was reported [40]. These dendrimers were synthesized for enhancing the blood brain barrier (BBB) transportation and improving the drug accumulation in the brain glioma cells. In a recent study amphiphilic Janus dendrimers consisting polar acidic amino acids and nonpolar naproxen molecules as the peripheral groups have been synthesized for bone-targeted drug delivery system [41]. These dendrimers take advantage of a dendritic display to carry multiple drug molecules and targeting moieties simultaneously.

Amphiphilic Janus dendrimers with low molecular weight were reported to readily form mechanically robust hydrogels when injected into aqueous solutions at very low mass proportion [42]. The injected dendrimers self-assembled as hierarchical fibrous

architectures with fibers in the nanoscopic range, which bundled together to form larger fibers in the mesoscopic range. The hydrogels also displayed remarkable mechanical properties, which could be further fine-tuned by modulating the position or number of hydrophobic alkyl chains in the dendrimer structure; thus, establishing a detailed structure–property relationship. Moreover, these gels could be loaded with different molecular weight bioactive compounds, ranging from small-molecule drugs to peptides or proteins, while retaining their biological activity.

Recently, Nanostructures based on ammonium-terminated amphiphilic Janus dendrimers were reported as camptothecin carriers with antiviral activity [43]. The self-assembly in water of these amphiphilic Janus dendrimers leads to micelles suitable to encapsulate camptothecin and act as therapy against the hepatitis C virus, HCV. Dendrimers consist of bis-MPA dendrons linked by their focal point through a CuAAC reaction. The hydrophilic dendron wears ammonium groups in its periphery whereas the lipophilic dendrons contain stearic acid chains. The morphology of the aggregates was controlled through the chemical structure of the dendrimers, particularly their molecular weight and the adequate combination of the lipophilic and hydrophilic blocks. Camptothecin-loaded dendrimer aggregates constitute effective systems to inhibit HCV replication and show low toxicity working at low drug concentrations.

From these literature precedence, it is feasible that the self-assembling amphiphilic dendrons and twin and Janus supramolecular dendrimers derived from them can be used as powerful structure-directing motifs for building new supramolecular architecture, generating new self-assembly mechanism and are suitable candidate for the synthesis of a new class of functional nanostructured materials.

1.6 Objectives of the current work

Although all the advantages of Percec-type amphiphilic dendrons, they have a limitation. That is higher generation dendrons can only adopt conical shape which self-assemble as explained before into supramolecular sphere dendrimers that self-organize into three-dimensional cubic lattices (Figure 11).

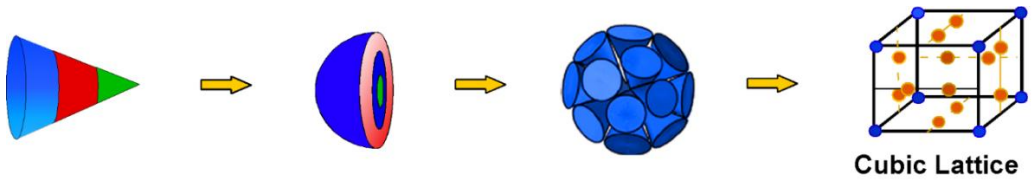


Figure 11 Self-assembly of higher generations amphiphilic dendrons.

To overcome this limitation, a modification of the dendrimer skeletal is required. This can be achieved by forming twin dendrimers or Janus dendrimers consisting of two different dendrons (Figure 7). The difference in Janus dendrimers can be only in the dendrons generations or they can have different chemical structure. This will increase the structure diversity of the supramolecular dendrimers without going to higher generations. So, the ultimate goal of this work is to synthesize a library of new twin and Janus dendrimers based on self-assembling amphiphilic dendrons.

The specific objectives of the current work are the following:

1. Rational design and synthesis of self-assembling wedge-shape amphiphilic mono-dendrons with different alkyl chains on the periphery of the dendrons.

2. Synthesis and characterization of new libraries of twin and Janus dendrimers.

3. Structural analysis of the supramolecular Janus-dendrimers in isolated and self-assembled state.

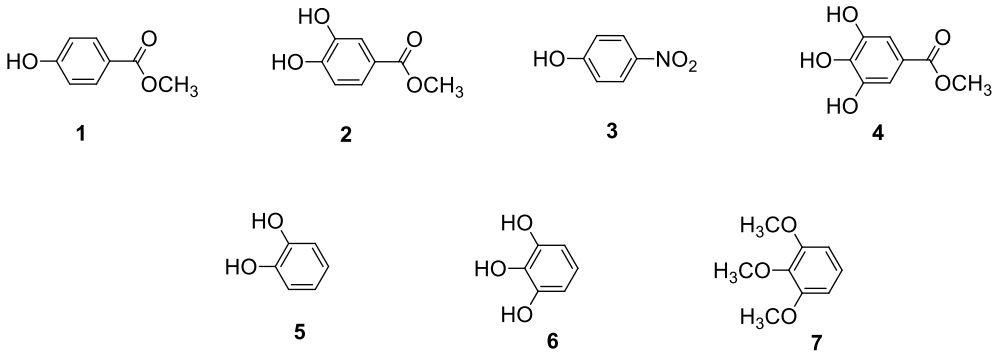
4. Material property measurements, such as thermal stability, gelation property and liquid crystalline behavior of the supramolecular nanomaterials.

CHAPTER 2

RESULTS AND CONCLUSION

2.1 Synthesis of dendritic precursors and dendritic building blocks

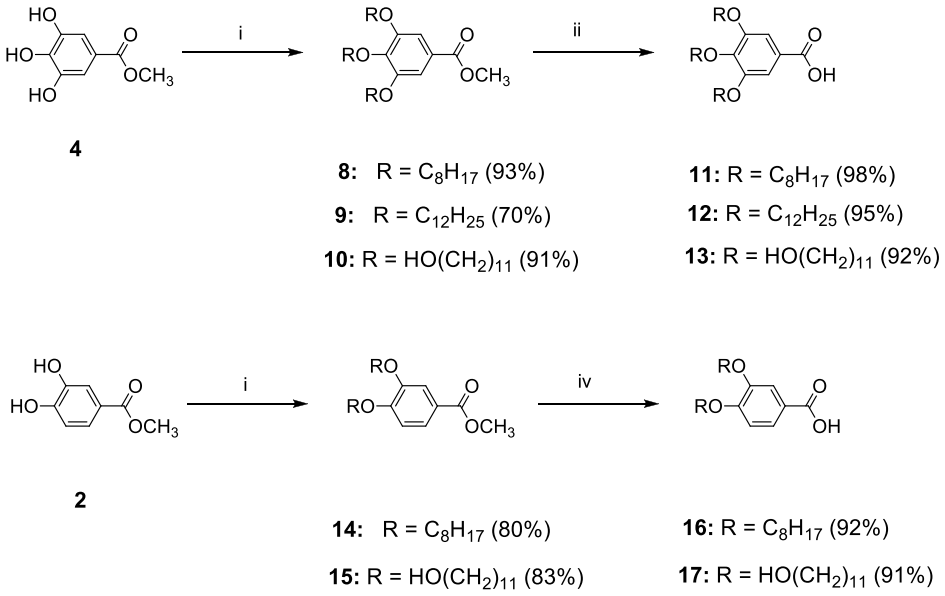
Scheme 1 illustrates the structures of seven different dendritic precursors that have been used to synthesize the required dendritic building blocks. Methyl 4-hydroxybenzoate (**1**), 4-nitrophenol (**3**), 1,2-dihydroxybenzene (**5**), 1,2,3-trihydroxybenzene (**6**) and 1,2,3-trimethoxybenzene (**7**) are all commercially available and have been procured. Methyl 3,4-dihydroxybenzoate (**2**), methyl 3,4,5-trihydroxybenzoate (**4**) were synthesized from the corresponding acids (commercially available) by Fisher esterification in refluxing CH_3OH using H_2SO_4 as catalyst.



Scheme 1 Structures of dendritic precursors.

2.1.1 Synthesis of dendritic acids

Scheme 2 outlines the synthesis of a library of first generation AB_3 and AB_2 type dendritic acids. The first step of the synthetic procedure involves the alkylation of methyl 3,4-dihydroxybenzoate (**2**) and methyl 3,4,5-trihydroxybenzoate (**4**) with the alkyl bromides in presence of potassium carbonate to give the esters. The dendritic acids were then obtained by the hydrolysis of the esters using KOH in refluxing ethanol and subsequent neutralization of the intermediate salts.



Reagents and conditions: (i) R-Br, K_2CO_3, DMF, 80 °C, 8 h; (ii) KOH, EtOH (95%), reflux, 2 h.

Scheme 2 Synthesis of first generation dendritic acids.

Compounds **11** (3,4,5)8G1-COOH, **12** (3,4,5)12G1-COOH and **16** (3,4)8G1-COOH are containing hydrophobic groups on the periphery of the dendritic acids, while compounds **13** (3,4,5)OH-11G1-COOH and **17** (3,4)OH-11G1-COOH are containing hydrophilic groups on the periphery.

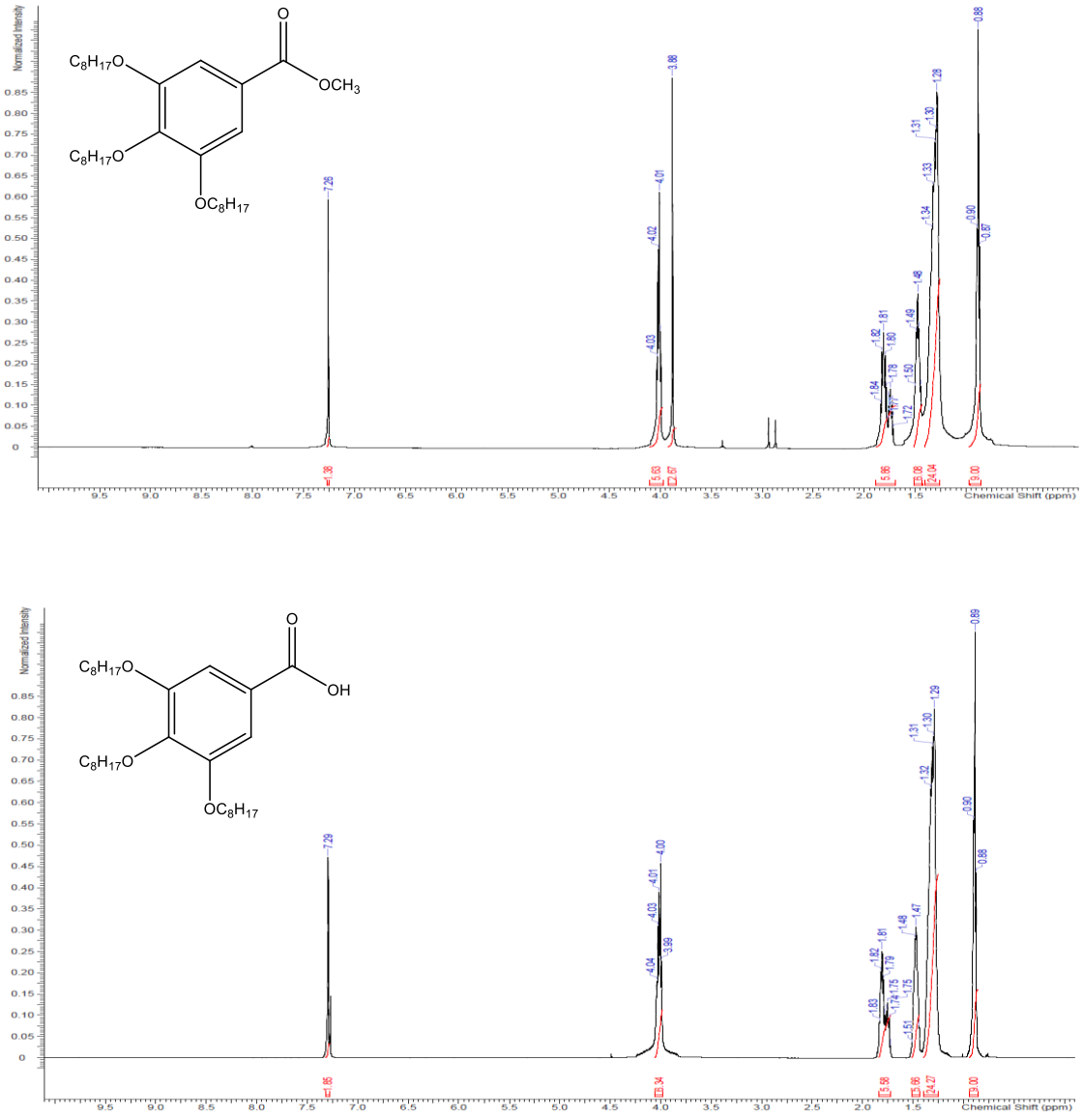
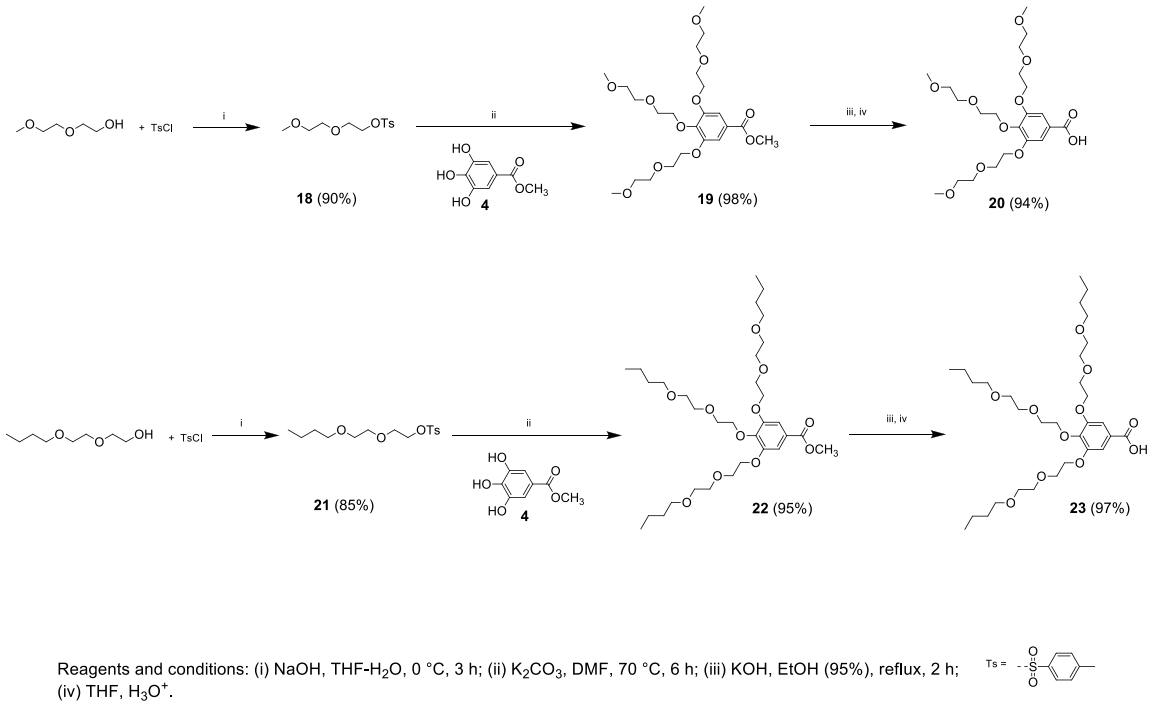


Figure 12 ^{1}H NMR spectra for compounds 8 (top) and 11 (bottom) in $CDCl_3$.

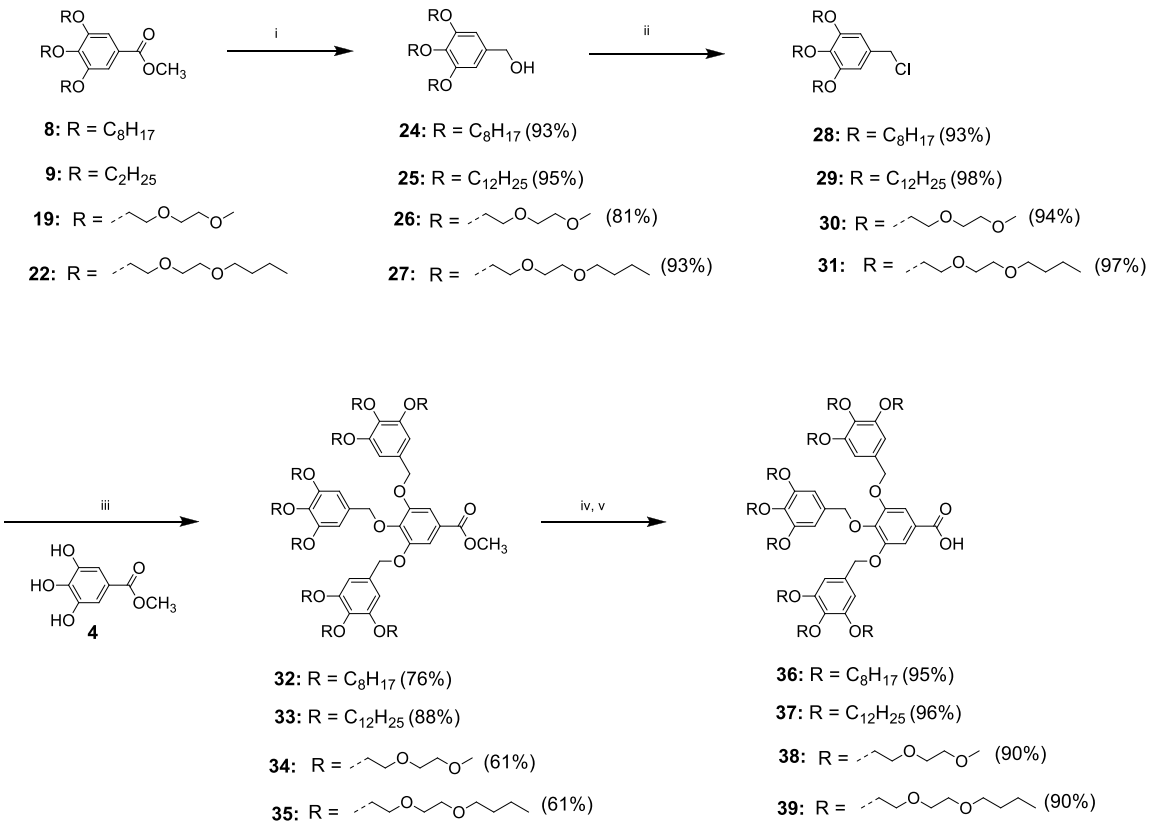
Figure 12 shows ^{1}H NMR spectra of compounds **8** and **11** in $CDCl_3$. The methyl ester protons can be identified at 3.88 ppm in compound **8** spectrum, where after hydrolysis, the methyl protons disappear in the spectrum of acid **11**. In both spectra the aromatic protons appear as a singlet at 7.26-7.29 ppm.



Scheme 3 Synthesis of first generation dendritic acids containing oligo(ethylene oxide) chains on the periphery.

Scheme 3 outlines the synthesis of other first generation AB_3 type dendritic acids containing oligo(ethylene oxide) chains on the periphery **20** (3,4,5)-2EO-(OMe)-G1-COOH and **23** (3,4,5)-2EO-(OBu)-G1-COOH. The first step involves reaction of diethylene glycol methyl ether and diethylene glycol butyl ether respectively with 4-toluenesulfonyl chloride in presence of sodium hydroxide to give the corresponding

tosylate salt. Then, the reaction of the tosylate salts with methyl 3,4,5-trihydroxybenzoate (**4**) in presence of potassium carbonate produced the esters. Finally, hydrolysis of the esters using KOH in refluxing ethanol and subsequent neutralization of the intermediate salts yielded the desired dendritic acids.



Reagents and conditions: (i) $LiAlH_4$, THF, 0 °C-r.t. 2 h; (ii) $SOCl_2$, CH_2Cl_2, 0 °C- RT, 1/2 h; (iii) K_2CO_3, DMF, 70 °C, 8 h; (iv) KOH, EtOH (95%), reflux, 2 h; (v) THF, H_3O^+.

Scheme 4 Synthesis of second generation dendritic acids.

Scheme 4 outlines the synthesis of a library of second generation AB_3 type dendritic acids containing both hydrophobic chains on the periphery **36** $(3,4,5)^2$8G2-COOH and **37** $(3,4,5)^2$12G2-COOH and oligo(ethylene oxide) chains as well **38** $(3,4,5)^2$-2EO-(OMe)-G2-COOH and **39** $(3,4,5)^2$-2EO-(OBu)-G2-COOH using a convergent iterative method. The first step of this synthetic procedure involves reduction of the first-generation dendritic esters (**8**, **9**, **19** and **22**) using $LiAlH_4$ in THF, then chlorination of the products (**24-27**) using $SOCl_2$ dissolved in DCM to give dendrons containing a benzyl chloride at their apex (**28-31**) respectively. Reaction of the benzyl chloride dendrons (**28-31**) with methyl 3,4,5-trihydroxybenzoate (**4**) in presence of potassium carbonate produced the second-generation dendritic esters (**32-35**) respectively. Finally, the desired dendritic second-generation acids were obtained by hydrolysis of the esters using KOH in refluxing ethanol and subsequent neutralization of the intermediate salts.

Figure 13 shows ^{1}H NMR spectra of compounds **32** and **34** in $CDCl_3$. In both spectra, the benzylic methylene protons appear at 5.02-5.04 ppm, the aromatic protons of the branching layer appear at 6.61-6.65 ppm and the aromatic protons ortho to the ester group appear at 7.32-7.38 ppm.

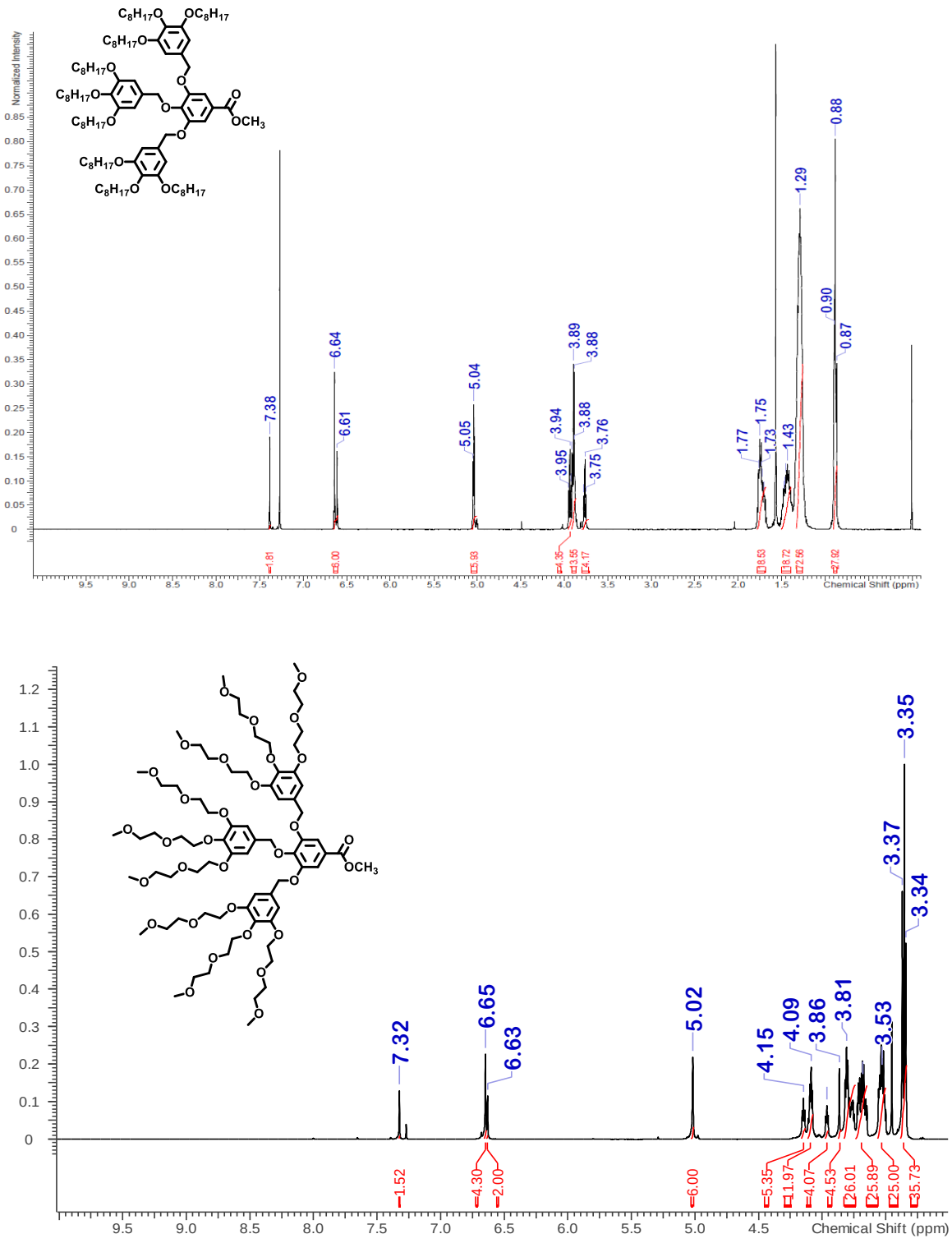
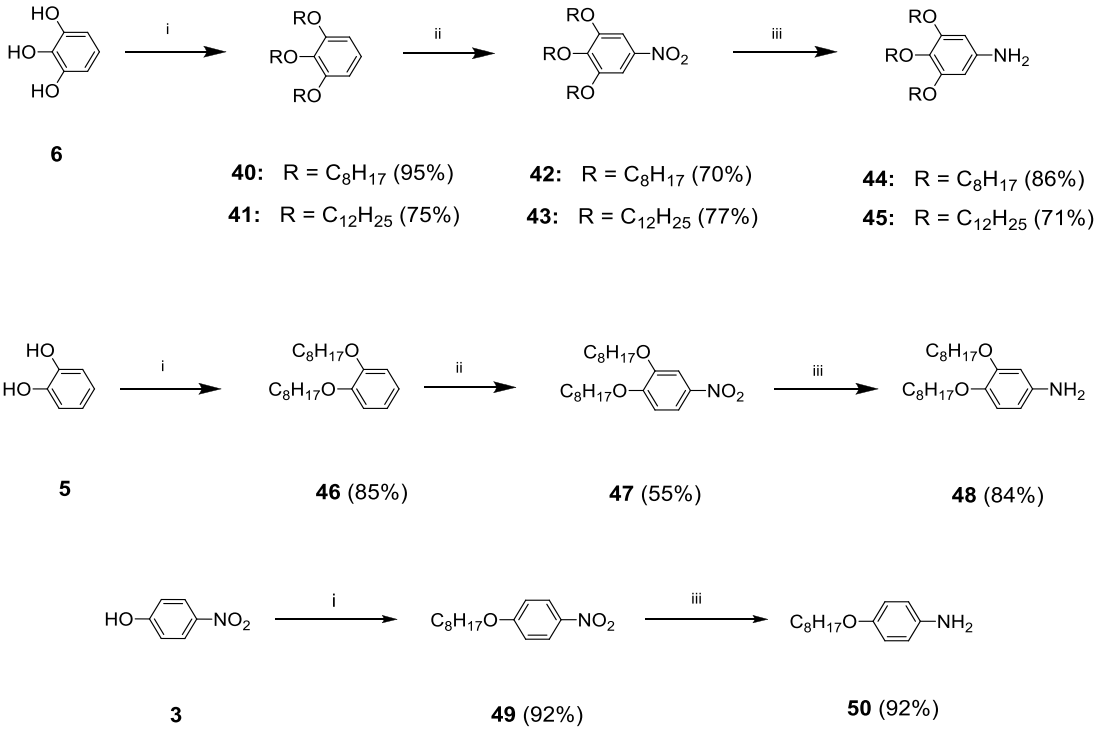


Figure 13 ^{1}H NMR spectra for compounds 32 (top) and 34 (bottom) in $CDCl_3$.

2.1.2 Synthesis of dendritic amines

Scheme 5 outlines the synthesis of dendritic amines using the dendritic precursors **5** and **6** as shown in scheme 1. Synthesis of dendritic amines **44** (3,4,5)8G1-NH_2 and **45** (3,4,5)12G1-NH_2 was accomplished by alkylation of 1,2,3-trihydroxybenzene (**6**) with the chosen alkyl bromides in DMF using K_2CO_3 followed by the nitration of the intermediate compounds **40** and **41** with HNO_3 supported on SiO_2 and subsequent reduction of nitro compounds **42** and **43** by hydrazine over graphite powder in ethanol.



Reagents and conditions: (i) R-Br, K_2CO_3, DMF, 80 °C, 8 h; (ii) CH_2Cl_2, SiO_2 .HNO_3, 22 °C, 15 min; (iii) NH_2NH_2 . H_2O, graphite, EtOH, reflux, 24 h.

Scheme 5 Synthesis of first generation dendritic amines.

Similarly, the dendritic amine **48** (3,4)8G1-NH_2 was synthesized using the dendritic precursor 1,2-dihydroxybenzene (**5**) following the same synthetic procedure. Compound **50** (4)8G0-NH_2 was synthesized by alkylation of 4-nitrophenol (**3**) with 1-bromooctane in DMF using K_2CO_3 followed by reduction of the nitro compound **49** by hydrazine over graphite powder in ethanol.

Figure 14 shows ^{1}H NMR spectra of compounds **40, 42** and **44** in $CDCl_3$. The ^{1}H NMR spectrum of the intermediate **40** shows that the aromatic protons appear as two peaks at 6.56 and 6.92 ppm, while after nitration with HNO_3 supported on SiO_2 the aromatic protons have been shifted downfield and appeared as a singlet peak at 7.47 ppm as shown in the ^{1}H NMR spectrum of **42** confirming that the nitration occurs selectively on one position. After reduction of the nitro compound **42** with hydrazine hydrate, the aromatic protons have been shifted upfield to 5.92 ppm as shown in the ^{1}H NMR spectrum of **44**.

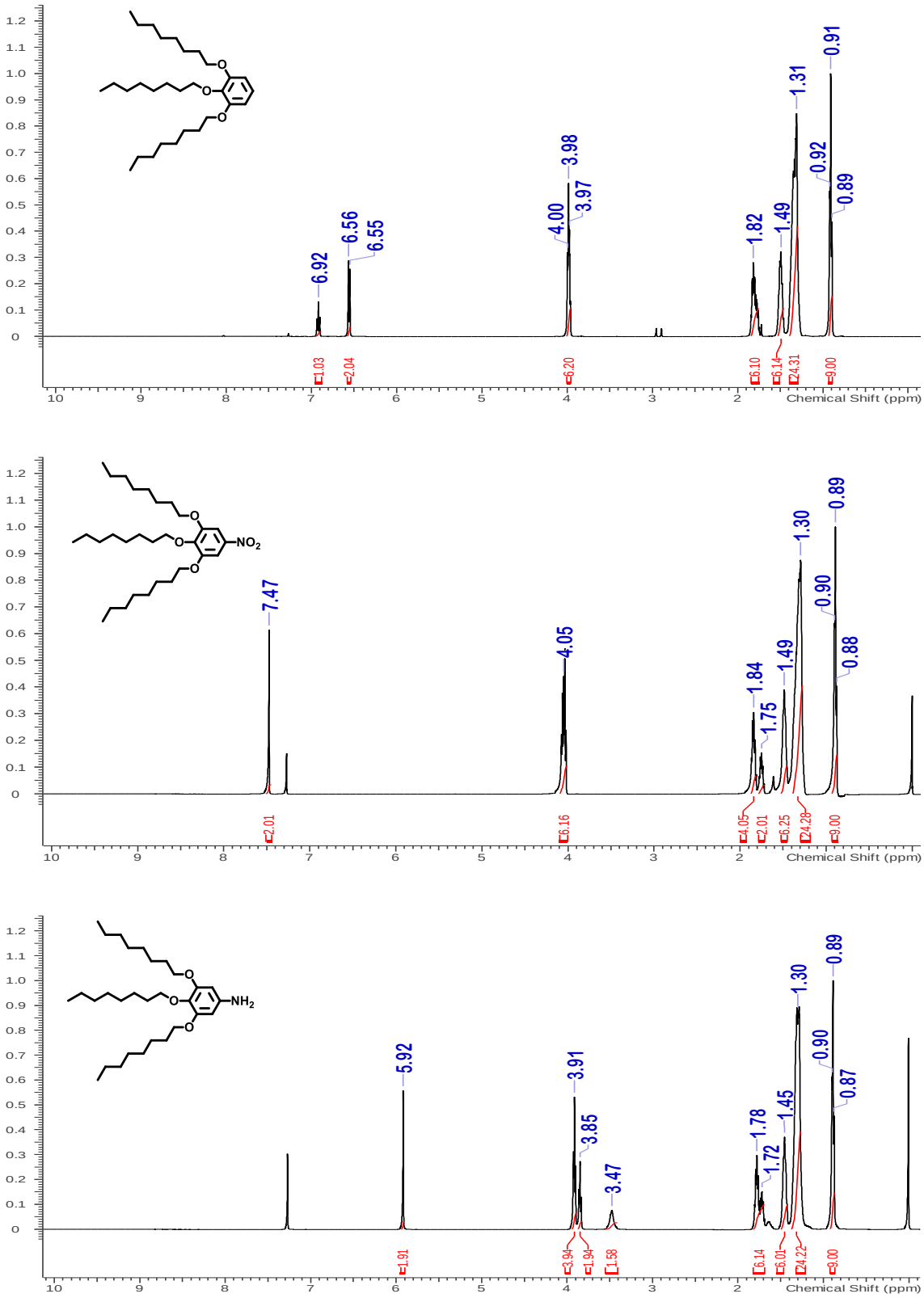
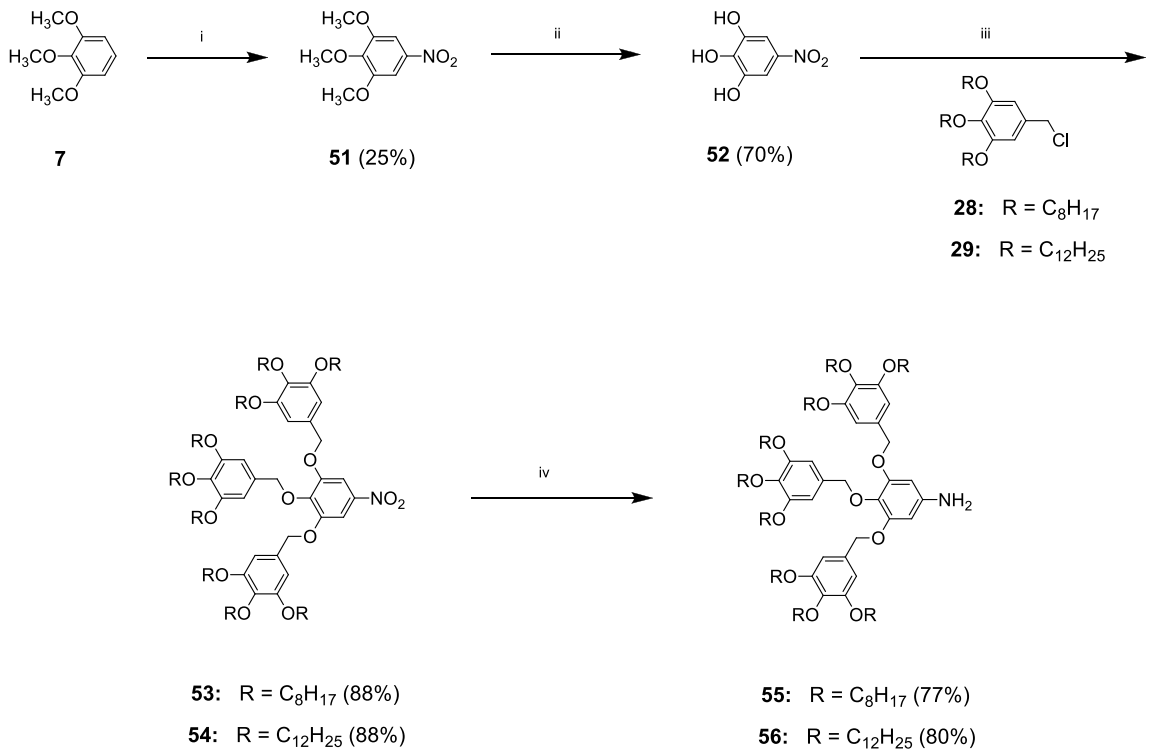


Figure 14 ^{1}H NMR spectra for compounds 40 (top), 42 (middle) and 44 (bottom) in $CDCl_3$.



Reagents and conditions:(i) CH_2Cl_2, SiO_2 .HNO_3, 22 °C, 15 min; (ii) Py . HCl, 200 °C, 1 h; (iii) K_2CO_3, DMF, 70 °C, 8 h; (iv) NH_2NH_2 . H_2O, graphite, EtOH, reflux, 24 h.

Scheme 6 Synthesis of second generation dendritic amines.

Scheme 6 outlines the synthesis of second generation dendritic amines **55** $(3,4,5)^2$8G2-NH_2 and **56** $(3,4,5)^2$12G2-NH_2. The first step of this synthetic procedure involves nitration of dendritic precursor 1,2,3-trimethoxybenzene (**7**) with HNO_3 supported on SiO_2. The resulted nitro compound **51** was then mixed with pyridine hydrochloride and stirred at 200 °C for 1 hour to give compound **52**. Alkylation of compound **52** with dendritic benzyl chlorides **28** and **29** using K_2CO_3 in DMF produced nitro compounds **53** and **54** respectively. The desired second generation dendritic amines were obtained by

reduction of the nitro compounds **53** and **54** by hydrazine over graphite powder in ethanol.

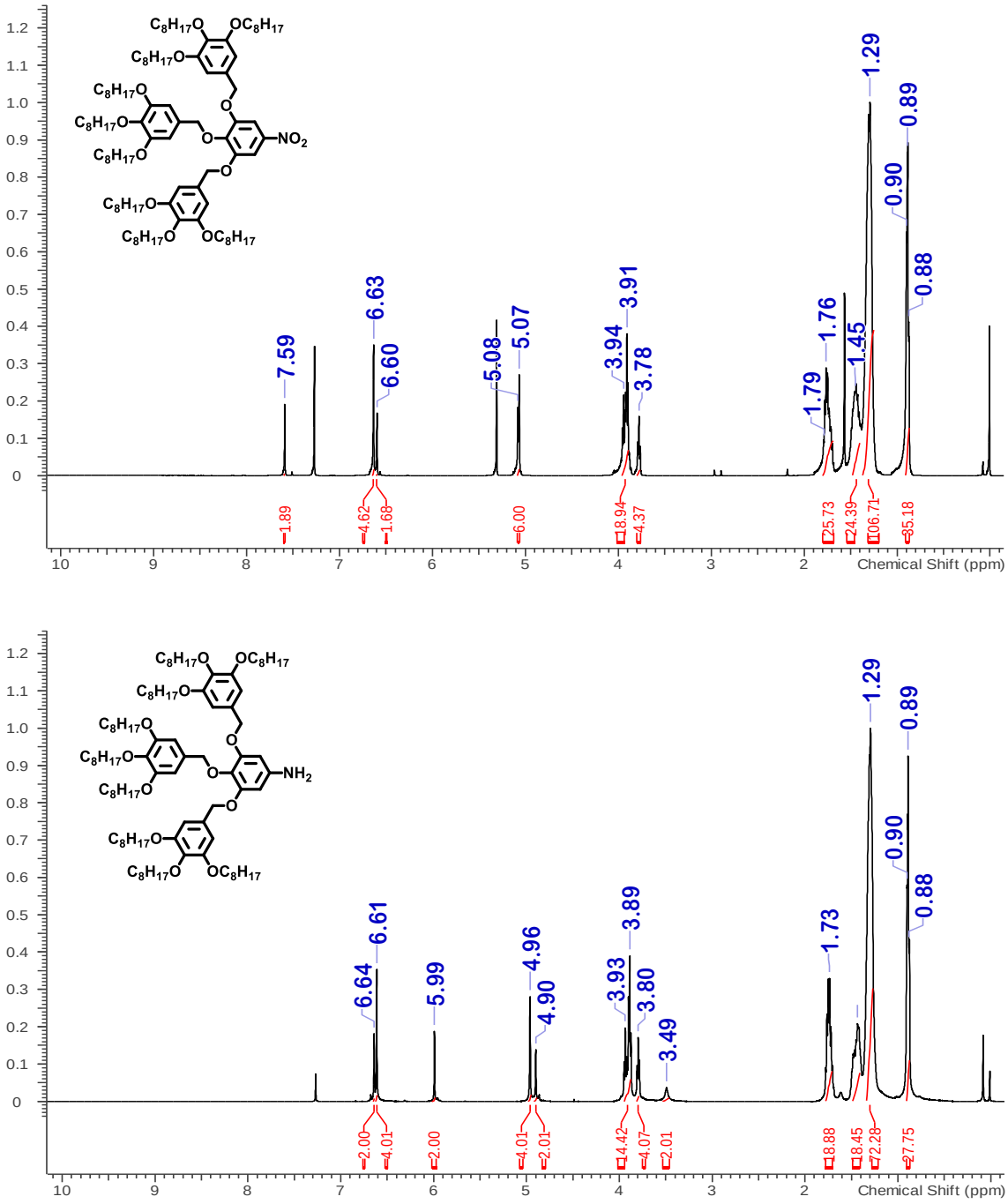


Figure 15 ^{1}H NMR spectra for compounds 53 (top) and 55 (bottom) in $CDCl_3$.

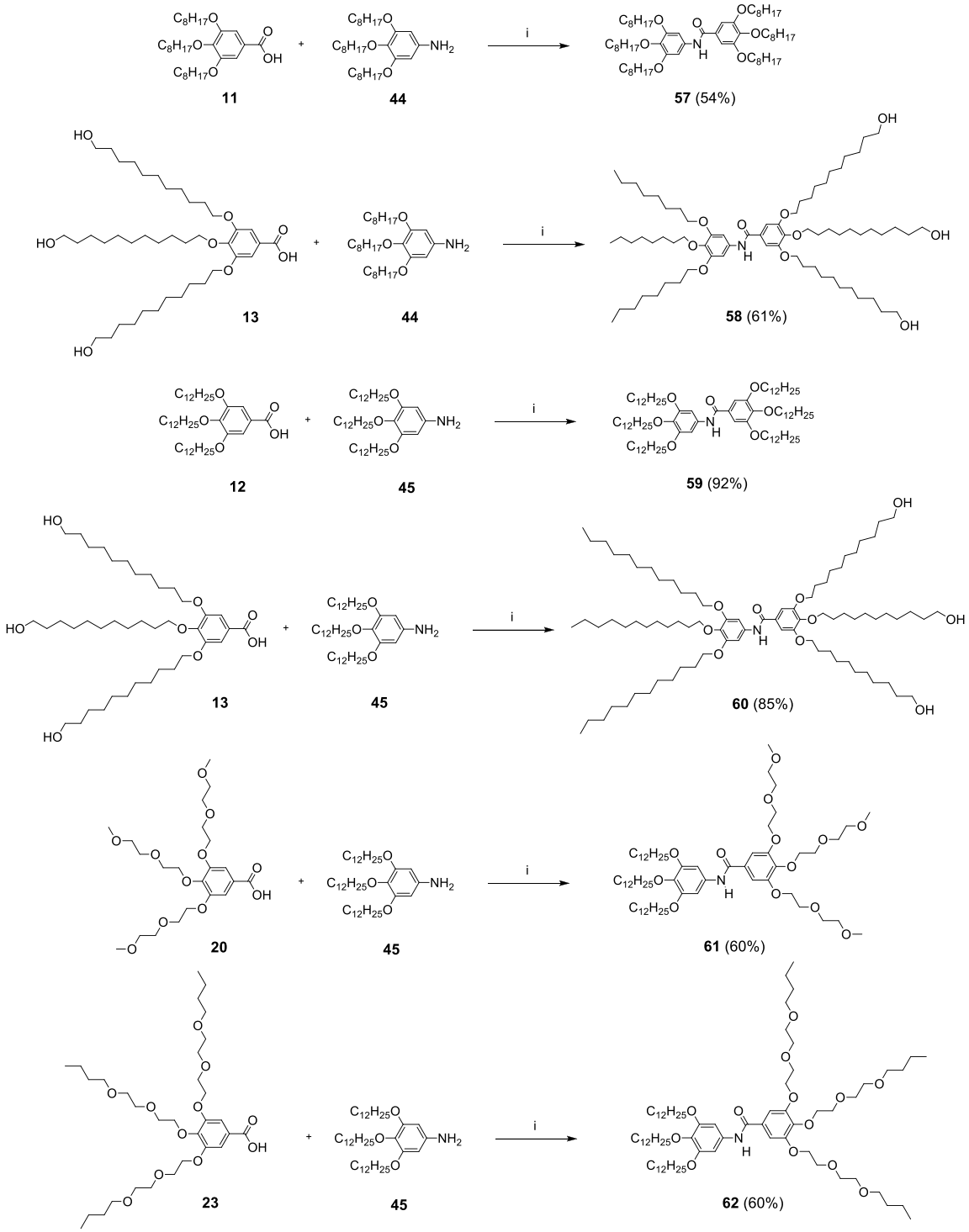
Figure 15 shows ^{1}H NMR spectra of compounds **53** and **55** in $CDCl_3$. In both spectra, the benzylic methylene protons appear at 4.90-5.08 ppm, the aromatic protons of the branching layer appear at 6.60-6.64 ppm while upon reduction, the aromatic protons ortho to the apex group have been shifted upfield from 7.59 ppm in nitro compound **53** to 5.99 ppm in the amine **55**.

2.2 Synthesis of supramolecular twin and Janus dendrimers

Successful synthesis of compounds as illustrated in schemes 2-6 has provided access to a large number of dendritic building blocks (dendritic acids and dendritic amines) that have been utilized to prepare various supramolecular Janus and twin dendrimers.

Scheme 7 outlines the synthesis of various supramolecular Janus and twin dendritic benzamides based on first generation AB_3 dendritic building blocks. Reaction of dendritic acids **11** and **12** with amines **44** and **45** in the presence of CDMT/NMM at room temperature produced the twin dendrimers **57** and **59** respectively having the same structural motifs on both sides of the amide bond. While amidation of **13** with amines **44** and **45** under the same reaction conditions gave the Janus dendrimers **58** and **60** respectively having two different structural motifs attached to each other by the amide bond.

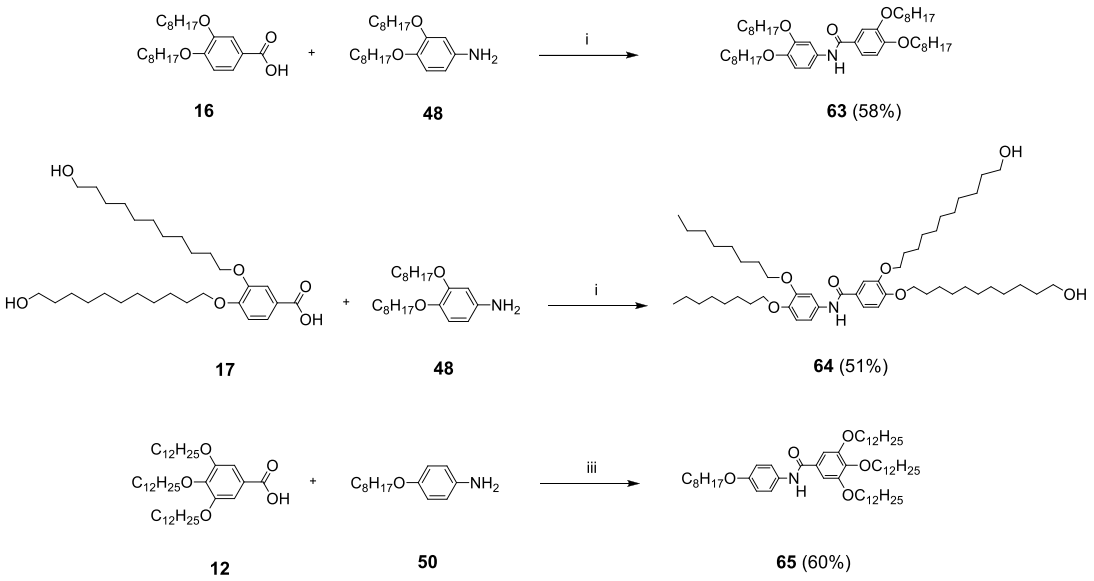
Similarly, Janus dendrimers **61** and **62** were synthesized by reaction of dendritic acids **20** and **23** bearing oligo(ethylene oxide) chains on the periphery with amine **45** bearing hydrophobic chains on the periphery under the same reaction conditions.



Reagents and condition: (i) CDMT, NMM, 25 ^{o}C.

Scheme **7 Synthesis of supramolecular Janus and twin dendrimers.**

Scheme 8 outlines the synthesis of other supramolecular dendritic benzamides. Twin dendrimer **63** and Janus dendrimer **64** were synthesized by coupling of first generation AB_2 dendritic building blocks. Reaction of dendritic acid **12** and amine **50** produced the Janus dendrimer **65** with different number of branching units on each side of the amide bond.



Scheme 8 Synthesis of dendritic benzamides.

Figure 16 shows ^{1}H NMR spectra of some of the synthesized benzamide dendrimers, compounds **57, 58** and **62** in $CDCl_3$. In the three spectra, the aromatic protons ortho to NH appear at 6.90-6.95 ppm, the aromatic protons ortho to CO appear at 7.03-7.19 ppm and the NH proton appears at 7.58-7.92 ppm.

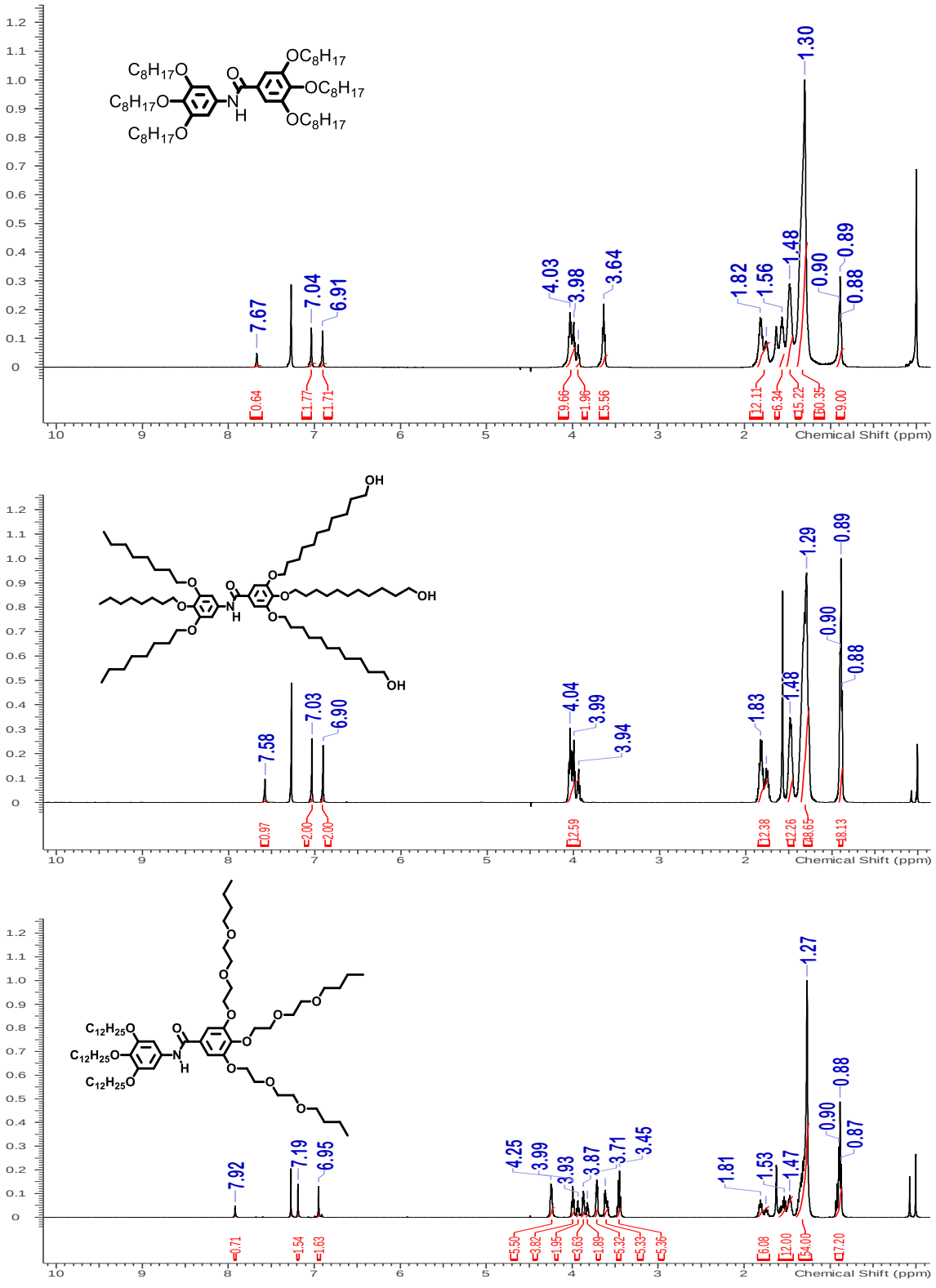
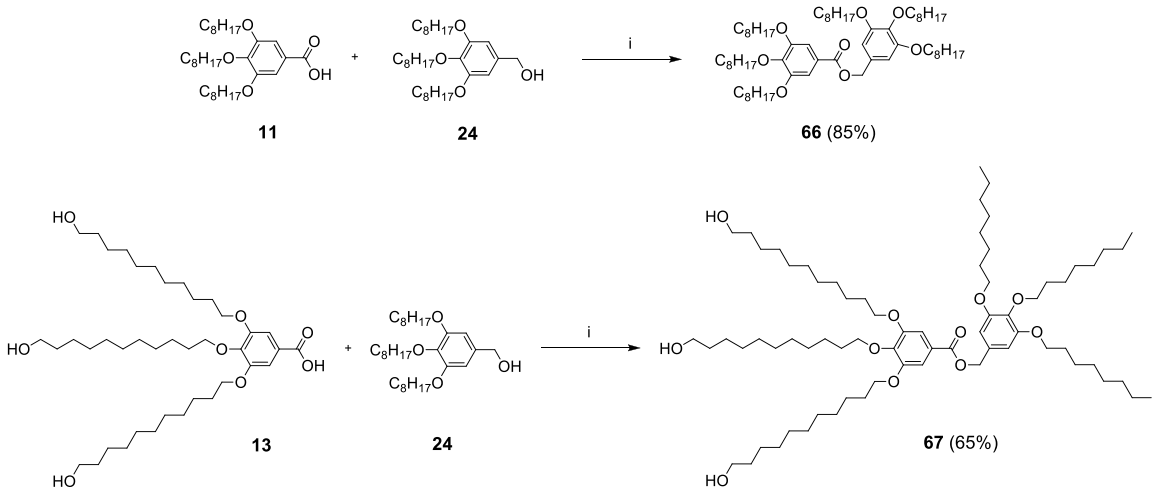


Figure 16 ^{1}H NMR spectra for compounds 57 (top), 58 (middle) and 62 (bottom) in $CDCl_3$.

Scheme 9 outlines the synthesis of supramolecular dendritic esters **66** and **67**. Reaction of dendritic acid **11** and dendritic benzyl alcohol **24** in the presence of DCC/DPTS at room temperature produced the twin dendritic ester **66**. While reaction of 13 and 24 under the same reaction conditions produced the Janus dendritic ester **67**.



Scheme 9 Synthesis of dendritic esters.

The ^{1}H NMR spectrum of compound **66** is shown in figure 17. The benzylic methylene protons appear at 5.24 ppm, the aromatic protons ortho to methylene appear at 6.63 ppm and the aromatic protons ortho to CO appear at 7.29 ppm.

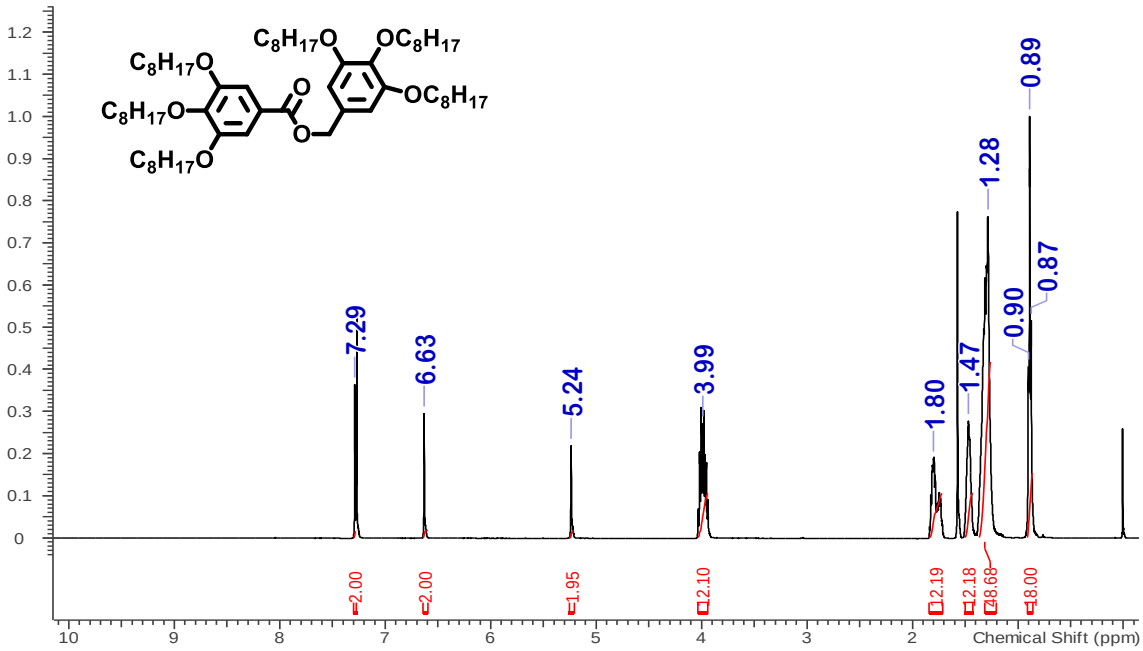
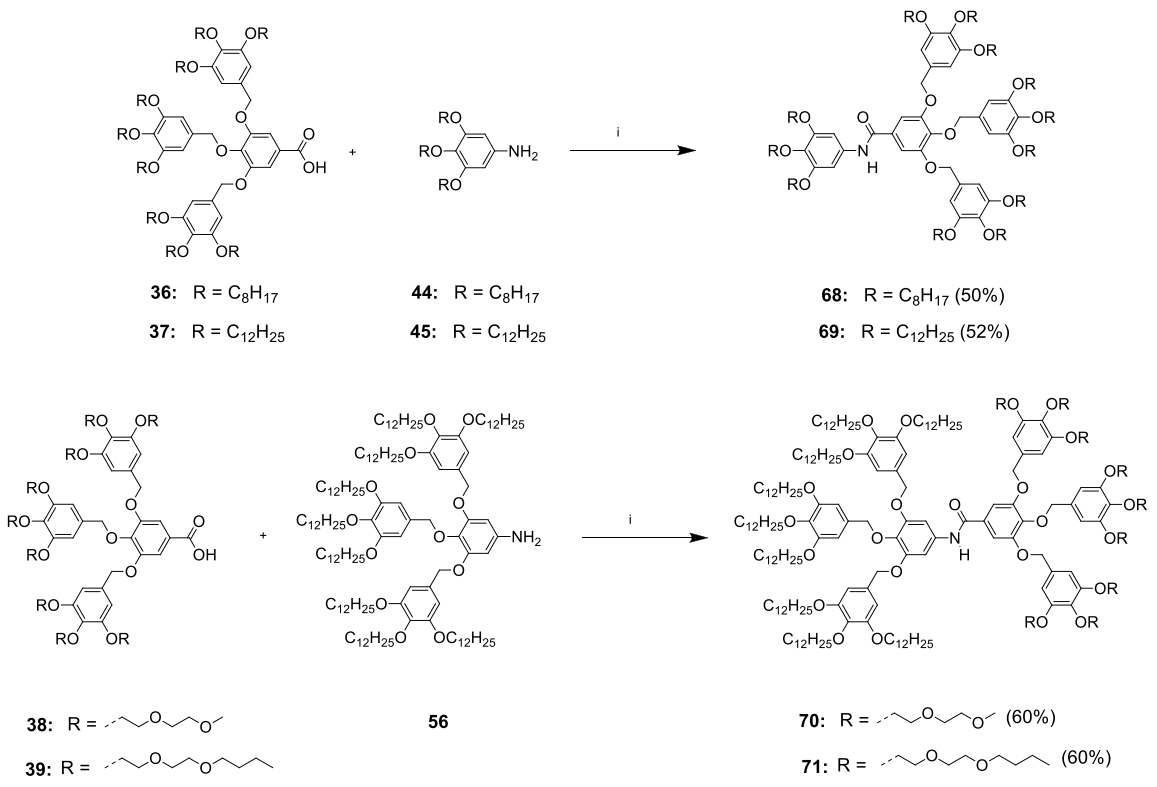


Figure 17 ^{1}H NMR spectrum for compounds 66 in $CDCl_3$.

Scheme 10 outlines the synthesis of higher generation supramolecular dendritic benzamides. Reaction of second generation dendritic acid **36** $(3,4,5)^2$8G2-COOH and first generation dendritic amine **44** (3,4,5)8G1-NH_2 in the presence of CDMT/NMM at room temperature produced Janus dendrimer **68**, where the difference is only in the dendron generation. Similarly, coupling of **37** $(3,4,5)^2$12G2-COOH and **45** (3,4,5)12G1-NH_2 under same reaction conditions produced Janus dendrimer **69**.

Amidation of dendritic acids **38** $(3,4,5)^2$-2EO-(OMe)-G2-COOH and **39** $(3,4,5)^2$-2EO-(OBu)-G2-COOH with dendritic amine **56** $(3,4,5)^2$12G2-NH_2 produced supramolecular second-generation Janus dendrimers **70** and **71** respectively.



Reagents and conditions: (i) CDMT, NMM, THF, 25 °C, 6 h.

Scheme 10 Synthesis of higher generation Janus dendrimers.

Figure 18 shows ^{1}H NMR spectra of compounds **69** and **70** in $CDCl_3$. The NH proton appears downfield at 7.46 ppm and 7.97 ppm respectively. Then the aromatic protons ortho to CO appear at 7.14 ppm and 7.17 ppm respectively, and the aromatic protons ortho to NH appear at 6.86 ppm and 7.09 ppm respectively. The analysis of the remaining peaks is explained in detail in the experimental section.

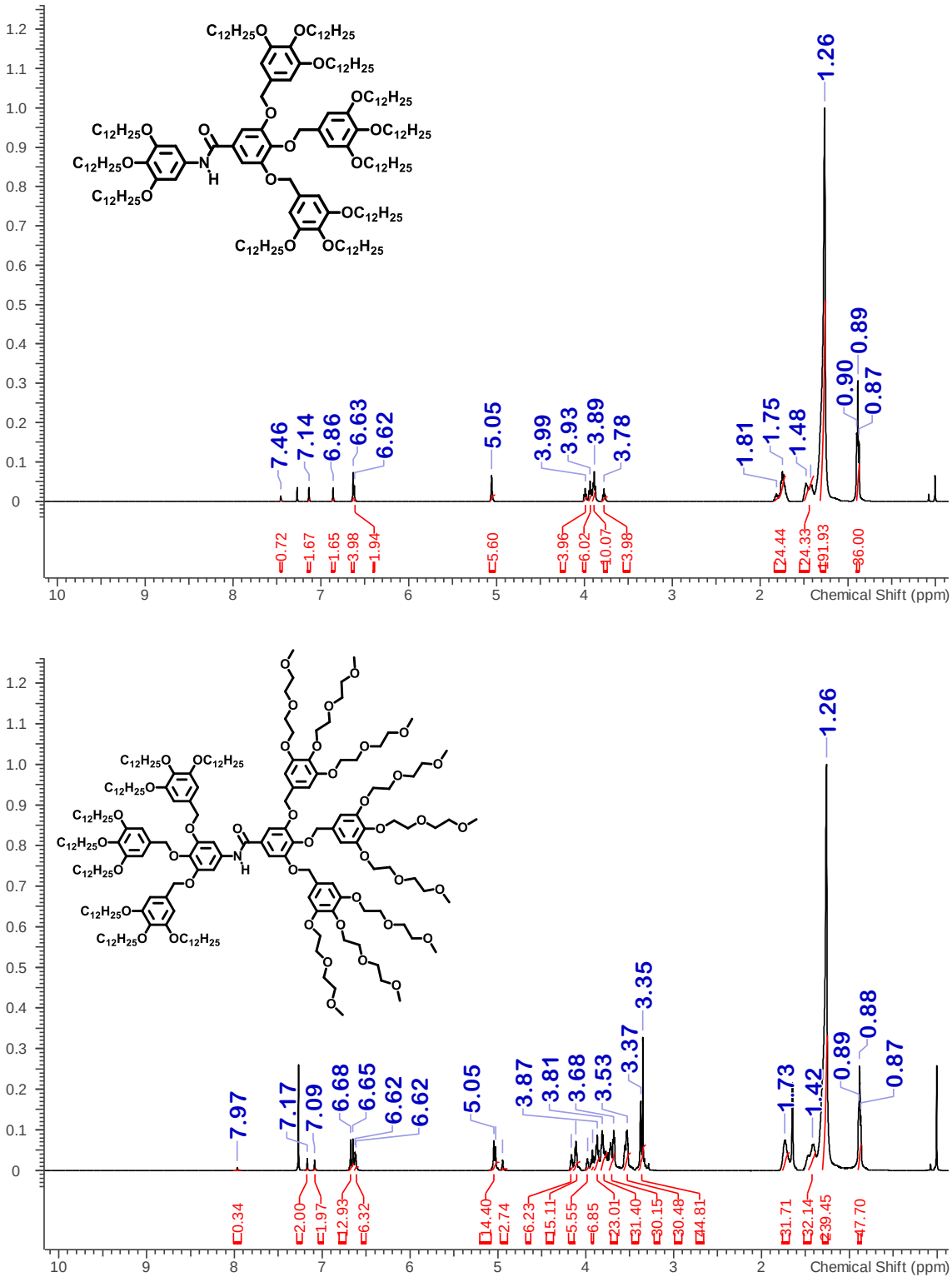


Figure 18 ^{1}H NMR spectra for compounds 69 (top) and 70 (bottom) in $CDCl_3$.

2.3 Structural analysis and material properties of dendrimers

All compounds have been characterized using ^{1}H and ^{13}C NMR (see experimental section and appendix). Structural analysis, self-assembly and liquid crystalline behavior was studied using a combination of differential scanning calorimetry (DSC) and thermal optical polarized microscopy (TOPM) techniques. Transition temperatures were determined by DSC at a rate of 10 °Cmin^{-1} and the assignment of phases was done by TOPM. Thermal stability was studied by thermal gravimetric analysis (TGA) technique. The gelation behavior was explored in various polar and nonpolar solvents.

2.3.1 Thermal gravimetric analysis (TGA)

Thermal gravimetric analysis (TGA) of all the dendrimers has shown that they are stable compounds with less than 5% weight loss at 350 °C for most of the dendrimers. Figure 19 shows TGA graphs for some dendrimers, compounds **57**, **66** and **69**. The graphs illustrate that benzamide dendrimer **57** has higher decomposition temperature than ester dendrimer **66** and higher generation benzamide **69**.

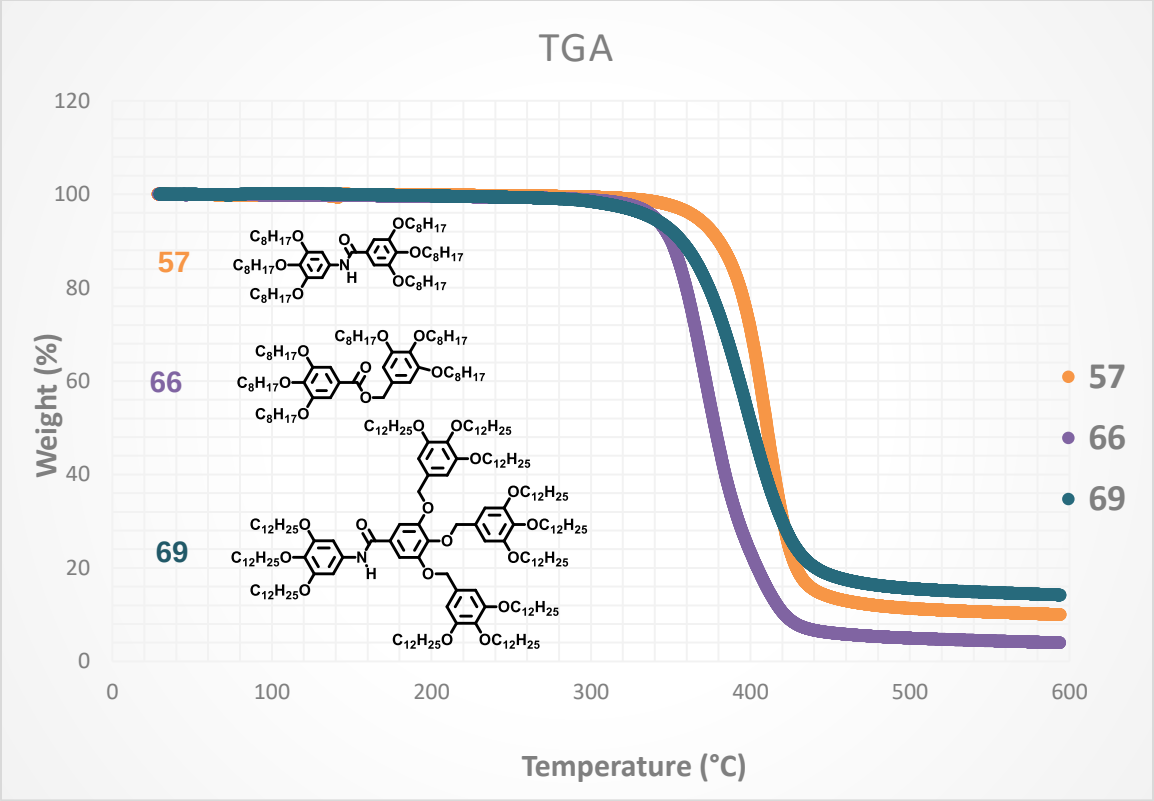


Figure 19 TGA graphs for compounds 57, 66 and 69.

Table 1 illustrates the isotropic temperatures (T_i) and decomposition temperatures (T_d) for the synthesized dendrimers. The isotropic temperature is the temperature at which the solid compound changes to liquid and was determined by DSC technique, while the decomposition temperature was determined by TGA at 5% weight loss.

It can be noticed from the table that first-generation benzamide dendrimers have higher decomposition temperatures. This can be attributed to the well-defined self-assembly of the dendrimers due to the hydrogen bonding stack of the amide linkage, while ester dendrimers exhibit low decomposition temperatures which may be attributed to the imperfect self-assembly due to the lack of hydrogen bonding. Moreover, higher

generation dendrimers have lower decomposition temperatures which may be attributed to the decomposition of some of the peripheral chains as the branching increases.

Table 1 Isotropic and decomposition temperatures of dendrimers.

Compound	Name	T_i	T_d
57	(3,4,5)8G1-(3,4,5)8G1-BzA	141	366
58	(3,4,5)8G1-(3,4,5)11OHG1-BzA	94	369
59	(3,4,5)12G1-(3,4,5)12G1-BzA	121	360
60	(3,4,5)12G1-(3,4,5)11OHG1-BzA	107	365
61	(3,4,5)12G1-(3,4,5)-2EO-(OMe)-G1-BzA	50	364
62	(3,4,5)12G1-(3,4,5)-2EO-(OBu)-G1-BzA	54	361
63	(3,4)8G1-(3,4)8G1-BzA	114	362
64	(3,4)8G1-(3,4)11OHG1-BzA	103	367
66	(3,4,5)8G1-(3,4,5)8G1-BzE	45	340
67	(3,4,5)8G1-(3,4,5)11OHG1-BzE	72	288
69	$(3,4,5)^2$12G1-$(3,4,5)^2$12G2-BzA	64	338
70	$(3,4,5)^2$12G2-$(3,4,5)^2$-2EO-(OMe)-G2-BzA	58	310

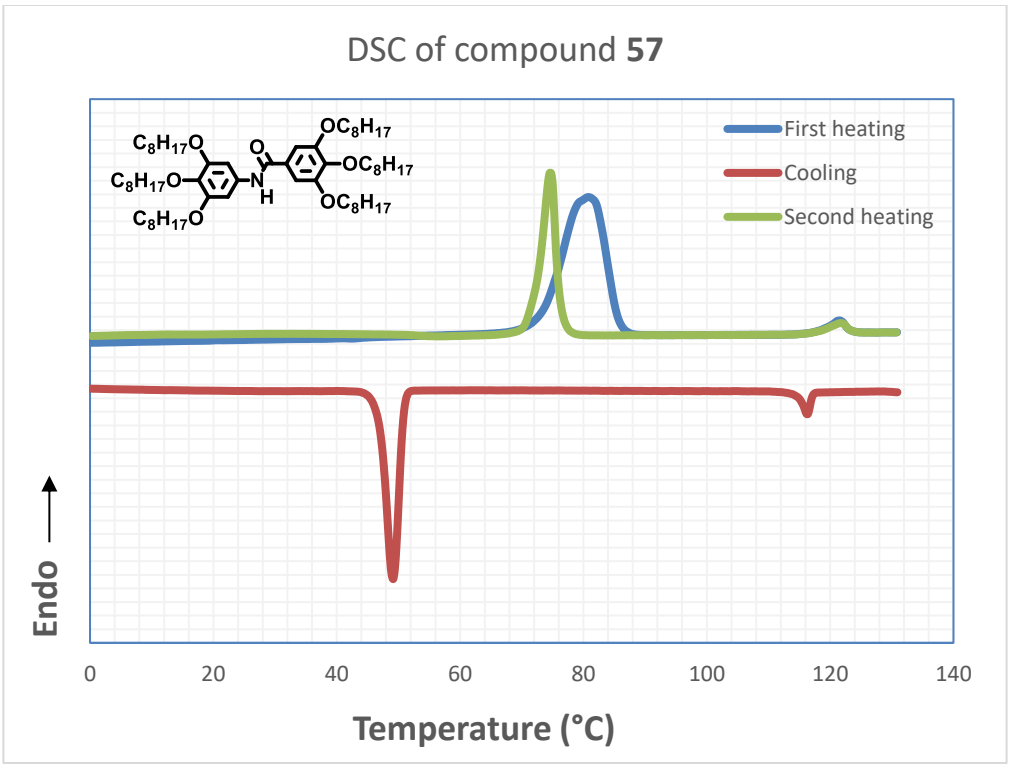
2.3.2 Differential scanning calorimetry (DSC)

Dendrimers have also been analyzed using differential scanning calorimetry (DSC) technique. Figure 20 shows the DSC graphs for benzamide **57** and ester **66**.

For benzamide **57**, three cycles can be identified; first heating, cooling and second heating. In the first heating cycle, a phase transition from the crystalline phase to liquid crystalline (LC) phase occurs at 80 °C. The LC phases have also been identified using thermal optical polarized microscope (TOPM) technique. Then, a phase transition from LC phase to isotropic phase occurs at 121 °C. The isotropic phase is the phase at which the compound changes to liquid. Thus, the LC phase is a phase in between the crystalline solid and the isotropic liquid states. The material may flow like a liquid, but its molecules are oriented in a crystal-like way.

In the cooling cycle, the LC phase was obtained at 116 °C then the material crystallizes at 49 °C. The second heating shows the same behavior as the first heating with slight difference in the LC phase transition.

While the DSC graph of compound **66** didn't show any LC phase transitions.



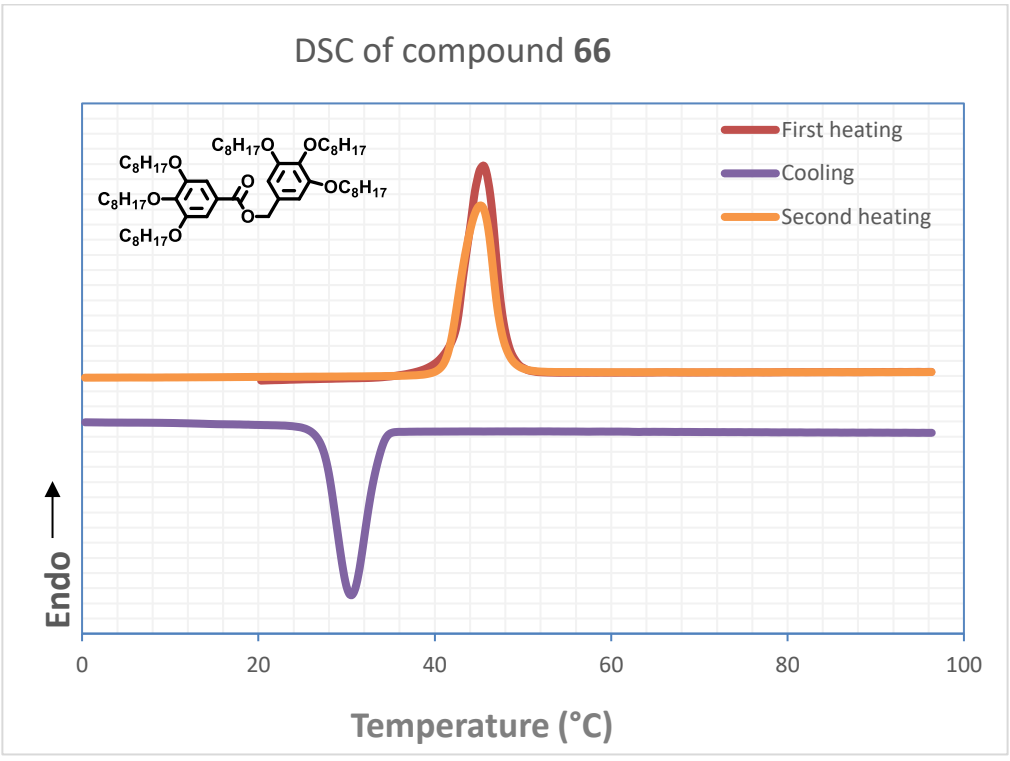


Figure 20 DSC graphs of compounds 57 and 66.

Table 2 summarizes the phase transitions in [°C] and the corresponding enthalpy changes in [kcal mol^{-1}] for the synthesized dendrimers. For instance, in the first heating of compound **57**, a phase transition occurs from crystalline phase (k) to liquid crystalline phase (LC) at 80.7 °C and the enthalpy change of this transition is 31.93 kcal mol^{-1}.

Table 2 Thermal characterization of dendrimers by DSC.

Phase transition [°C] and corresponding enthalpy changes [kcal mol^{-1}]		
Compound	**Heating**	**Cooling**
57	k 80.7 (31.93) LC 121.4 (1.32) i	i 116.3 (-1.16) LC 49.1 (-13.40) k
	k 74.6 (13.96) LC 121.6 (1.10) i	
58	K 75.4 (8.79) LC 107.4 (17.67) i	i 76.4 (-16.38) k
	k 34.4 (0.96) LC 107.6 (17.21) i	
59	k_1 14.3 (1.10) k_2 63.9 (22.13) LC 141.6 (1.28) i	i 137.3 (-1.00) LC 44.3 (-6.78) k_2 25.8 (-1.44)
	k_1 30.4 (1.84) k_2 62.4 (7.39) LC 141.6 (1.05) i	
60	k_1 82.1 (6.96) k_2 96.4 (13.10) i	i 73.3 (-13.92) k
	k 94.7 (14.74) i	
61	k 50.6 (16.63) i	i 27.5 (-15.31) k
	k 47.6 (15.05) i	
65	k_1 54.8 (0.65) k_2 73.4 (17.01) i	i 8.4 (-11.97) k
	k 24.19 (0.78) -k 56.7 (9.66) LC 69.4 (0.27) i	
66	k 45.4 (16.89) i	i 30.5 (-12.67) k
	k 45.2 (13.61) i	
67	k_1 44.1 (0.28) k_2 72.1 (16.56) i	i 55.5 (-17.94) k
	k_1 41.3 (0.77) k_2 73.7 (17.11) i	
69	k_1 45.01 (1.00) k_2 66.83 (24.05) i	i 58.9 (-1.63) LC 40.1 (-21.52) k
	k 30.79 (8.48) -k 63.5 (30.64) i	
70	k 58.1 (39.95) i	i -6.1 (-5.61) k_2 -23.9 (-0.94) k_1
	k_1 2.4 (5.46) k_2 53.7 (14.55) i	

2.3.3 Thermal optical polarized microscope (TOPM) textures

Figure 21 shows thermal optical polarized microscope (TOPM) textures of some dendrimers obtained by cooling from isotropic phase at a rate of 1 °Cmin^{-1}. The textures indicate that the dendrimers self-assemble into columnar assemblies, because spherical lattices will not give any textures.

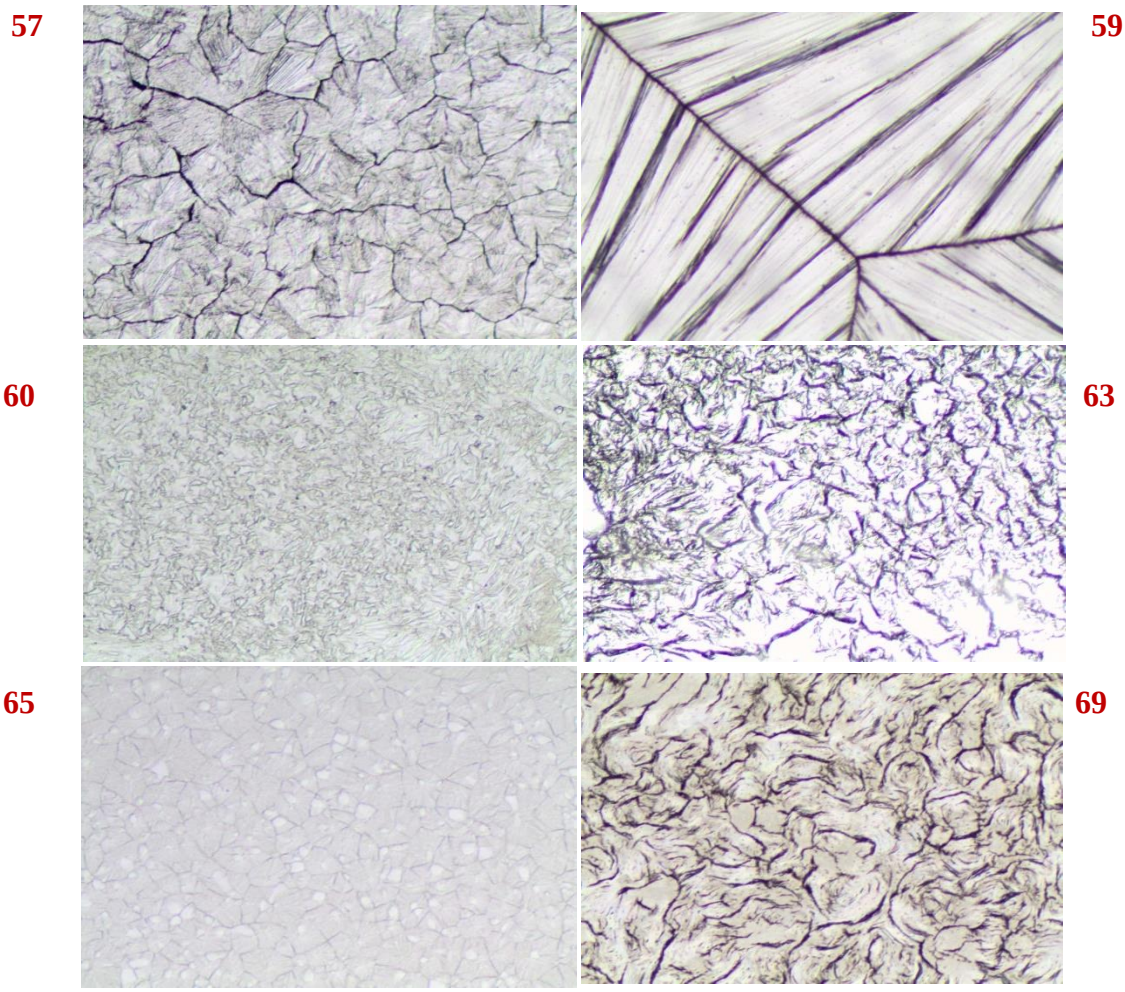


Figure 21 Representative TOPM textures obtained by cooling at a rate of 1 °Cmin^{-1} from isotropic phase of 57, 59, 60, 63, 65 and 69.

2.3.4 Gelation properties of dendrimers

Due to the amphiphilic nature of the synthesized supramolecular twin and Janus dendrimers, they can form thixotropic gel in both polar and nonpolar environment and self-assemble in micellar structure. Gelation behavior of the dendrimers has been investigated in various solvents at a concentration of 10 mg/mL as shown in table 3.

Table 3 Gelation behavior of dendrimers in different solvents, G= Clear Gel, TG= Turbid Gel, P= Precipitate, S= Soluble, I= Insoluble.

Compound	MeOH	EtOH	DCM	THF	Toluene	Benzene	Hexane	$CHCl_3$	Et_2O	EtOAc	iso-PrOH	H_2O
57	TG	I	S	S	S	S	S	S	S	S	P	I
58	TG	P	TG	S	G	TG	TG	S	P	P	S	I
59	I	TG	S	S	S	S	P	S	P	TG	TG	I
60	TG	P	TG	S	G	TG	TG	S	P	P	S	I
61	TG	TG	S	S	TG	G	P	S	P	TG	S	I
62	P	P	S	S	G	TG	P	S	P	TG	P	I
63	P	TG	S	S	S	S	P	S	P	TG	TG	I
64	TG	P	TG	S	G	TG	TG	S	P	P	S	I
66	I	TG	S	S	S	S	P	S	P	TG	TG	I
67	P	P	TG	S	TG	TG	TG	S	P	TG	S	I
70	I	TG	S	S	G	G	TG	S	P	P	S	I
71	P	TG	S	S	G	P	P	S	TG	P	P	I

It was found that toluene gives the best clear organogel for most of the dendrimers. Organogels are useful in applications such as drug delivery mediums for topical and oral pharmaceuticals, organic application mediums for cosmetics, cleaning materials for art conservation, delivery mediums and/or nutrients in nutraceuticals (vitamins and supplements), particles in personal care products (shampoo, conditioner, soap, toothpaste, etc.) and a crystalline fat alternative in food processing.

Figure 22 shows the organogels formed compounds **58**, **60**, **62**, **64** and **70** in toluene at a concentration of 10 mg/mL.

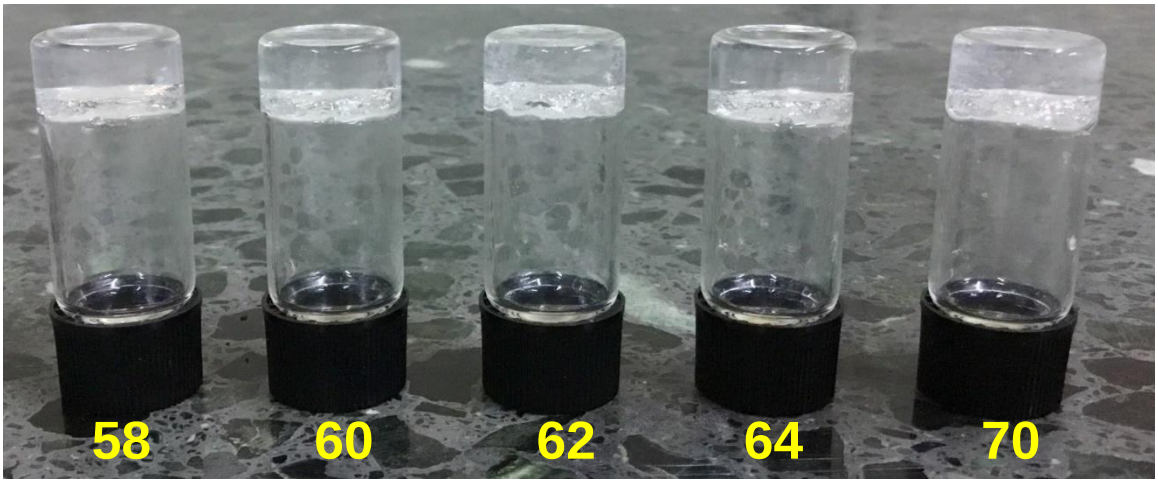


Figure 22 Organogels formed from compounds 58, 60, 62, 64 and 70 in toluene.

Furthermore, the critical gel concentration (which is the minimum concentration at which a stable gel is formed) has been investigated in selected solvents as shown in table 4. It was found that some dendrimers can form a stable gel at a minimum concentration of 1.5 mg/mL.

Table 4 Critical gel concentration of the dendrimers in selected solvents.

Compound	Solvent	CGC
57	Methanol	5.0 mg/mL
58	Toluene	4.5 mg/mL
59	Ethanol	1.5 mg/mL
60	Toluene	4.0 mg/mL
61	Benzene	4.0 mg/mL
62	Toluene	3.0 mg/mL
63	Ethyl acetate	1.5 mg/mL
64	Toluene	3.0 mg/mL
66	Ethanol	2.0 mg/mL
67	Toluene	3.5 mg/mL
70	Benzene	2.5 mg/mL
71	Toluene	2.5 mg/mL

2.4 Conclusion

New supramolecular twin and Janus dendrimers based on self-assembling amphiphilic dendrons have been synthesized. The structural analysis and thermal analysis of these supramolecular dendrimers was performed using TGA, DSC and TOPM techniques. The liquid crystalline behavior of the self-assembled state of the dendrimers has been studied. Finally, the gelation behavior of the dendrimers was studied.

CHAPTER 3

EXPERIMENTAL

3.1 General methods

Unless otherwise stated, all solvents and reagents were purchased from commercial suppliers and used without further purification. Tetrahydrofuran (THF) was freshly distilled prior to use from sodium/benzophenone ketyl under N_2. CH_2Cl_2 was freshly distilled from CaH_2.

All reactions were carried out under N_2 atmosphere unless otherwise stated. All reactions were monitored by thin layer chromatography (TLC) performed on pre-coated silica gel plates.

^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on a JEOL LA 500 instrument. Thermal optical polarized microscope (Olympus BX 43 integrated with hot stage) was used to identify the LC phases of the supramolecular dendrimers and the transition temperatures associated with the phase transitions. Differential scanning calorimetry (DSC) was used for structural analysis.

3.2 Synthesis

Methyl 3,4,5-tris(octyloxy)benzoate (8):

To a thoroughly degassed suspension of anhydrous K_2CO_3 (16.6 g, 0.12 mole) in DMF (100 mL) was added methyl gallate (3.70 g, 0.02 mole) and the reaction mixture was heated to 80 °C which was added 1-bromooctane (15.45 g, 0.08 mole) under N_2 atmosphere. After stirring for 8 h at 80 °C, the reaction mixture was poured into ice-cooled water and extracted with CH_2Cl_2. The CH_2Cl_2 extract was washed by H_2O and brine then dried over $MgSO_4$ and filtered. The solvent was removed in a rotatory evaporator and passed through a short column of basic Al_2O_3 using CH_2Cl_2 as eluent to give 9.8 g (93 %) as yellow oil. TLC (EtOAc/hexane = 1/9): R_f = 0.56; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.88 (t, 9H, C*H*$_3$, *J* = 6.56 Hz), 1.31 (overlapped m, 24H, $CH_3(CH_2)_4$), 1.47 (m, 6H, C*H*$_2$$(CH_2)_2O$), 1.79 (m, 6H, C*H*$_2$$CH_2O$), 3.88 (s, 3H, CO_2CH_3), 4.01 (m, 6H, C*H*$_2$O), 7.26 (s, 2H, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.11, 22.73, 26.12-30.18, 31.91, 52.07, 69.11, 73.42, 107.71, 124.59, 142.34, 152.81, 166.92.

Methyl 3,4,5-tris(dodecyloxy)benzoate (9):

To a thoroughly degassed suspension of anhydrous K_2CO_3 (9.0 g, 0.065 mole) in DMF (50 mL) was added methyl gallate (2.0 g, 0.011 mole) and the reaction mixture was heated to 80 °C which was added 1-bromododecane (10.8 g, 0.043 mole) under N_2 atmosphere. After stirring for 8 hours at 80 °C, the reaction mixture was poured into ice-cooled water and the precipitate was collected by filtration and vacuum dried. The crude product was passed through a short column of basic Al_2O_3 using CH_2Cl_2 as eluent.

Recrystallization from acetone yielded 5.2 g (70 %). TLC (EtOAc/hexane = 1/9): R_f = 0.51; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.88 (t, 9H, C*H*$_3$, *J* = 6.71 Hz), 1.27 (overlapped m, 48H, $CH_3(CH_2)_8$), 1.47 (m, 6H, C*H*$_2$$(CH_2)_2O$), 1.78 (m, 6H, C*H*$_2$$CH_2O$), 3.89 (s, 3H, CO_2CH_3), 4.01 (m, 6H, C*H*$_2$O), 7.26 (s, 2H, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.11, 22.73, 26.12-30.18, 31.91, 52.07, 69.11, 73.42, 107.71, 124.59, 142.34, 152.81, 166.92.

Methyl 3,4,5-tris(11-hydroxyundecyloxy)benzoate (10):

To a thoroughly degassed suspension of anhydrous K_2CO_3 (5.5 g, 0.04 mole) in DMF (50 mL) was added methyl gallate (1.22 g, 0.0066 mole) and the reaction mixture was heated to 80 °C which was added 11-bromo-1-undecanol (5.0 g, 0.02 mole) under N_2 atmosphere. After stirring for 8 hours at 80 °C, the reaction mixture was poured into ice-cooled water and the precipitate was collected by filtration and vacuum dried. The crude product was passed through a short column of basic Al_2O_3 using CH_2Cl_2 as eluent. Recrystallization from acetone yielded 4.2 g (91 %). TLC (EtOAc/hexane = 5/5): R_f = 0.26; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.31 (overlapped m, 36H, (C*H*$_2$)$_6$$CH_2CH_2OH$), 1.47 (m, 6H, C*H*$_2$$(CH_2)_2O$), 1.56 (m, 6H, C*H*$_2$$CH_2OH$), 1.77 (m, 6H, C*H*$_2$$CH_2O$), 2.16 (s, 3H, O*H*), 3.64 (t, 6H, C*H*$_2$OH, *J* = 6.56 Hz), 3.89 (s, 3H, CO_2CH_3), 4.01 (m, 6H, C*H*$_2$O), 7.25 (s, 2H, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 25.68, 25.70, 25.97, 26.00, 29.22, 29.29, 29.37, 29.41, 29.46, 29.48, 29.52, 29.54, 29.56, 29.60, 29.62, 30.24, 32.67, 52.08, 62.97, 62.99, 69.10, 73.44, 107.96, 124.68, 142.35, 152.85, 167.03.

3,4,5-Tris(octyloxy)benzoic acid (11):

Compound **8** (2.5 g, 0.0048 mole), EtOH (30 mL, 95%), and KOH (1.61 g, 0.029 mole) were placed into a 50 mL round-bottom flask containing a Teflon coated magnetic stirring bar and heated to reflux for 2 h under constant stirring. After the reaction was completed it was cooled to room temperature and acidified with dil. HCl (1 M) to pH 1. The reaction mixture was poured into ice-cooled water and then filtered and vacuum dried to yield 2.4 g (98 %). TLC (EtOAc/hexane = 1/9): R_f = 0.05; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.89 (t, 9H, C*H*$_3$, *J* = 6.87 Hz), 1.31 (overlapped m, 24H, $CH_3(CH_2)_4$), 1.47 (m, 6H, C*H*$_2$$(CH_2)_2O$), 1.79 (m, 6H, C*H*$_2$$CH_2O$), 4.03 (m, 6H, C*H*$_2$O), 7.29 (s, 2H, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.11, 22.73, 26.12-30.18, 31.91, 69.21, 73.62, 108.51, 123.69, 143.14, 152.91, 172.22.

3,4,5-Tris(dodecyloxy)benzoic acid (12):

Compound **9** (3.0 g, 0.0044 mole), EtOH (30 mL, 95%), and KOH (1.71 g, 0.03 mole) were placed into a 50 mL round-bottom flask containing a Teflon coated magnetic stirring bar and heated to reflux for 2 h under constant stirring. After the reaction was completed it was cooled to room temperature and acidified with dil. HCl (1 M) to pH 1. The reaction mixture was poured into ice-cooled water and then filtered and vacuum dried to yield 2.8 g (95 %). TLC (EtOAc/hexane = 1/9): R_f = 0.05; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.88 (t, 9H, C*H*$_3$, *J* = 6.71 Hz), 1.29 (overlapped m, 48H, $CH_3(CH_2)_8$), 1.47 (m, 6H, C*H*$_2$$(CH_2)_2O$), 1.80 (m, 6H, C*H*$_2$$CH_2O$), 4.02 (m, 6H, C*H*$_2$O), 7.32 (s, 2H, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.11, 22.73, 26.12-30.18, 31.91, 69.21, 73.62, 108.51, 123.69, 143.14, 152.91, 172.22.

3,4,5-Tris(11-hydroxyundecyloxy)benzoic acid (13):

Compound **10** (2.0 g, 0.0029 mole), EtOH (20 mL, 95%), and KOH (0.97 g, 0.017 mole) were placed into a 50 mL round-bottom flask containing a Teflon coated magnetic stirring bar and heated to reflux for 2 h under constant stirring. After the reaction was completed it was cooled to room temperature and acidified with dil. HCl (1 M) to pH 1. The reaction mixture was poured into ice-cooled water and then filtered and vacuum dried to yield 1.8 g (92 %). TLC (EtOAc/hexane = 5/5): R_f = 0.05; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.30 (overlapped m, 36H, (C*H*$_2$)$_6$$CH_2CH_2OH$), 1.48 (m, 6H, C*H*$_2$$(CH_2)_2O$), 1.57 (m, 6H, C*H*$_2$$CH_2OH$), 1.78 (m, 6H, C*H*$_2$$CH_2O$), 3.09 (s, 3H, O*H*), 3.65 (t, 3H, C*H*$_2$OH, *J* = 6.56 Hz), 4.04 (m, 6H, C*H*$_2$O), 7.31 (s, 2H, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 25.68, 25.70, 25.97, 26.00, 29.22, 29.29, 29.37, 29.41, 29.46, 29.48, 29.52, 29.54, 29.56, 29.60, 29.62, 30.24, 32.67, 62.97, 62.99, 69.10, 73.44, 108.96, 123.88, 143.35, 152.95, 173.23.

Methyl 3,4-bis(octyloxy)benzoate (14):

To a thoroughly degassed suspension of anhydrous K_2CO_3 (8.30 g, 0.06 mole) in DMF (60 mL) was added methyl-3,4-dihydroxybenzoate (2.52 g, 0.015 mole) and the reaction mixture was heated to 80 °C which was added 1-bromooctane (8.68 g, 0.045 mole) under N_2 atmosphere. After stirring for 8 h at 80 °C, the reaction mixture was poured into ice-cooled water and the product was filtered and dried. The product was purified through a short column of basic Al_2O_3 using CH_2Cl_2 as eluent followed by recrystallization from acetone to give 4.71 g (80 %). TLC (EtOAc/hexane = 1/9): R_f = 0.50; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.88 (t, 6H, C*H*$_3$, *J* = 6.55 Hz), 1.31 (overlapped m, 16H,

$CH_3(CH_2)_4$), 1.47 (m, 4H, $CH_2(CH_2)_2O$), 1.79 (m, 4H, CH_2CH_2O), 3.88 (s, 3H, CO_2CH_3), 4.01 (m, 4H, CH_2O), 6.93 (d, 1H, Ar*H* meta to $COOCH_3$, *J* = 8.55 Hz), 7.62 (dd, 1H, Ar*H*, *J* = 8.24 Hz), 7.65 (d, 1H, Ar*H*, *J* = 1.80 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.11, 22.73, 26.12-30.18, 31.91, 52.07, 69.11, 110.51, 112.65, 120.30, 123.56, 148.34, 154.71, 166.52.

Methyl 3,4-bis(11-hydroxyundecyloxy)benzoate (15):

To a thoroughly degassed suspension of anhydrous K_2CO_3 (5.53 g, 0.04 mole) in DMF (50 mL) was added methyl-3,4-dihydroxybenzoate (1.68 g, 0.01 mole) and the reaction mixture was heated to 70 °C which was added 11-bromo-1-undecanol (5.0 g, 0.02 mole) under N_2 atmosphere. After stirring for 8 hours at 70 °C, the reaction mixture was poured into ice-cooled water and the precipitate was collected by filtration and vacuum dried. The crude product was passed through a short column of basic Al_2O_3 using CH_2Cl_2 as eluent. Recrystallization from acetone yielded 4.22 g (83 %). TLC (EtOAc/hexane = 5/5): R_f = 0.25; ^1H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.30 (overlapped m, 24H, $(CH_2)_6CH_2CH_2OH$), 1.45 (m, 4H, $CH_2(CH_2)_2O$), 1.53 (m, 4H, CH_2CH_2OH), 1.76 (m, 4H, CH_2CH_2O), 2.59 (s, 2H, O*H*), 3.61 (t, 4H, CH_2OH, *J* = 6.56 Hz), 3.89 (s, 3H, CO_2CH_3), 4.02 (m, 4H, CH_2O), 6.98 (d, 1H, Ar*H* meta to $COOCH_3$, *J* = 8.50 Hz), 7.63 (dd, 1H, Ar*H*, *J* = 8.20 Hz), 7.65 (d, 1H, Ar*H*, *J* = 1.75 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 25.65, 25.71, 25.95, 26.03, 29.25, 29.31, 29.36, 29.42, 29.46, 29.49, 29.52, 29.54, 29.56, 29.60, 29.62, 30.26, 32.68, 52.08, 62.96, 62.99, 69.10, 73.14, 110.61, 112.67, 120.31, 123.59, 148.38, 154.74, 166.32.

3,4-Bis(octyloxy)benzoic acid (16):

Compound **14** (3.0 g, 0.00764 mole), EtOH (30 mL, 95%), and KOH (3.0 g, 0.05349 mole) were placed into a 50 mL round-bottom flask containing a Teflon coated magnetic stirring bar and heated to reflux for 2 h under constant stirring. After the reaction was completed it was cooled to room temperature and acidified with dil. HCl (1 M) to pH 1. The reaction mixture was poured into ice-cooled water and then filtered and vacuum dried to yield 2.7 g (92 %). TLC (EtOAc/hexane = 1/9): R_f = 0.05; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.88 (t, 6H, C*H*$_3$, *J* = 6.55 Hz), 1.31 (overlapped m, 16H, $CH_3(CH_2)_4$), 1.46 (m, 4H, C*H*$_2$$(CH_2)_2O$), 1.78 (m, 4H, C*H*$_2$$CH_2O$), 4.02 (m, 4H, C*H*$_2$O), 6.95 (d, 1H, Ar*H* meta to $COOCH_3$, *J* = 8.55 Hz), 7.61 (dd, 1H, Ar*H*, *J* = 8.24 Hz), 7.64 (d, 1H, Ar*H*, *J* = 1.80 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.15, 22.72, 26.05-30.10, 31.92, 69.04, 111.69, 112.55, 122.57, 123.86, 149.25, 155.46, 169.41.

3,4-Bis(11-hydroxyundecyloxy)benzoic acid (17):

Compound **15** (3.0 g, 0.0059 mole), EtOH (30 mL, 95%), and KOH (2.31 g, 0.0413 mole) were placed into a 50 mL round-bottom flask containing a Teflon coated magnetic stirring bar and heated to reflux for 2 h under constant stirring. After the reaction was completed it was cooled to room temperature and acidified with dil. HCl (1 M) to pH 1. The reaction mixture was poured into ice-cooled water and then filtered and vacuum dried to yield 2.65 g (91 %). TLC (EtOAc/hexane = 5/5): R_f = 0.05; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.31 (overlapped m, 24H, (C*H*$_2$$)_6CH_2CH_2OH$), 1.44 (m, 4H, C*H*$_2$$(CH_2)_2O$), 1.53 (m, 4H, C*H*$_2$$CH_2OH$), 1.76 (m, 4H, C*H*$_2$$CH_2O$), 2.19 (s, 2H, O*H*), 3.62 (t, 4H, C*H*$_2$OH, *J* = 6.55 Hz), 4.03 (m, 4H, C*H*$_2$O), 7.12 (d, 1H, Ar*H* meta to

$COOCH_3$, *J* = 8.55 Hz), 7.61 (dd, 1H, Ar*H*, *J* = 8.25 Hz), 7.66 (d, 1H, Ar*H*, *J* = 1.80 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 25.65, 25.71, 25.95, 26.03, 29.25, 29.31, 29.36, 29.42, 29.46, 29.49, 29.52, 29.54, 29.56, 29.60, 29.62, 30.25, 32.61, 62.91, 62.94, 69.11, 73.15, 110.68, 112.61, 120.30, 123.58, 148.35, 154.72, 169.42.

2-(2-Methoxyethoxy)ethyl 4-methylbenzenesulfonate (18):

To a 0 °C solution of diethylene glycol methyl ether (12.02 g, 0.10 mole) and NaOH (6.0 g, 0.15 mole) in THF (200 mL) and H_2O (40 mL), TsCl (21.0 g, 0.11 mole dissolved in 60 mL of THF) was added dropwise (the temperature was maintained below 5 °C). After complete addition, the reaction mixture was stirred at 0 °C for 3 hours. The reaction mixture was poured into cold water (100 mL) and extracted with CH_2Cl_2. The CH_2Cl_2 extract was washed by H_2O (pH = 1) and brine then dried over $MgSO_4$ and filtered. The solvent was removed in a rotatory evaporator and passed through a short column of silica gel using (EtOAc/Hexane = 5/5) as eluent to give 24.6 g (90 %) as colorless oil. TLC (EtOAc/Hexane = 5/5): R_f = 0.55; ^1H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.43 (s, 3H, PhC*H*$_3$), 3.34 (s, 3H, OC*H*$_3$), 3.47 (m, 2H, CH_3OCH_2), 3.56 (m, 2H, $CH_3OCH_2CH_2$), 3.68 (m, 2H, C*H*$_2$CH$_2$OTs), 4.16 (m, 2H, C*H*$_2$OTs), 7.33 (d, 2H, Ar*H*, *ortho* to CH_3, *J* = 8.24 Hz), 7.79 (d, 2H, Ar*H*, *meta* to CH_3, *J* = 8.24 Hz).

Methyl 3,4,5-tris(2-(2-methoxyethoxy)ethoxy)benzoate (19):

To a thoroughly degassed suspension of anhydrous K_2CO_3 (10.37 g, 0.075 mole) in DMF (60 mL) was added methyl gallate (2.30 g, 0.013 mole) and the reaction mixture was heated to 70 °C which was added compound **18** (10.29 g, 0.038 mole) under N_2 atmosphere. After stirring for 6 h at 70 °C, the reaction mixture was poured into ice-

cooled water and extracted with CH_2Cl_2. The CH_2Cl_2 extract was washed by H_2O, HCl (1 M) and brine then dried over $MgSO_4$ and filtered. The solvent was removed in a rotatory evaporator and passed through a short column of basic Al_2O_3 using CH_2Cl_2 as eluent to give 6.0 g (98 %) as pale-yellow oil. TLC (EtOAc/hexane = 7/3): R_f = 0.28; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 3.38 (s, 3H, C*H₃ para* to CO_2CH_3), 3.39 (s, 6H, C*H₃ meta* to CO_2CH_3), 3.56 (m, 6H, CH_3OCH_2), 3.72 (m, 6H, $CH_3OCH_2CH_2$), 3.82 (t, 2H, OCH_2CH_2 *para* to CO_2CH_3, *J* = 5.04 Hz), 3.88 (overlapped m, 7H, OCH_2CH_2 *meta* to CO_2CH_3, CO_2CH_3), 4.21 (t, 4H, OCH_2 *meta* to CO_2CH_3, *J* = 4.88 Hz), 4.25 (t, 2H, OCH_2 *para* to CO_2CH_3, *J* = 5.04 Hz), 7.30 (s, 2H, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 52.00, 58.86, 58.89, 68.66, 69.46, 70.29, 70.44, 70.59, 71.83, 71.88, 72.33, 108.78, 124.87, 142.37, 152.20, 166.53.

3,4,5-Tris(2-(2-methoxyethoxy)ethoxy)benzoic acid (20):

Compound **19** (4.41 g, 0.009 mole), EtOH (50 mL, 95%), and KOH (3.03 g, 0.054 mole) were placed into a 100 mL round-bottom flask containing a Teflon coated magnetic stirring bar and heated to reflux for 2 h under constant stirring. After the reaction was completed it was cooled to room temperature and diluted with THF (20 mL). The solution was acidified with glacial CH_3COOH to pH 3. The reaction mixture was poured into ice-cooled water and extracted with CH_2Cl_2. The CH_2Cl_2 extract was washed by H_2O and brine then dried over $MgSO_4$ and filtered. The solvent was removed in a rotatory evaporator to yield 4.02 g (94 %) of viscous red oil. TLC (EtOAc/hexane = 7/3): R_f = 0.05; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 3.37 (s, 3H, C*H₃ para* to CO_2H), 3.38 (s, 6H, C*H₃ meta* to CO_2H), 3.56 (m, 6H, CH_3OCH_2), 3.72 (m, 6H, $CH_3OCH_2CH_2$), 3.82 (t, 2H, OCH_2CH_2 *para* to CO_2H, *J* = 5.04 Hz), 3.88 (t, 4H, OCH_2CH_2 *meta* to

CO_2H, *J* = 4.88 Hz), 4.21 (t, 4H, OC*H*$_2$ *meta* to CO_2H, *J* = 4.88 Hz), 4.26 (t, 2H, OC*H*$_2$ *para* to CO_2H, *J* = 5.04 Hz), 7.34 (s, 2H, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 60.07, 60.10, 69.37, 70.68, 71.50, 71.65, 71.80, 73.04, 73.09, 73.54, 110.99, 127.78, 144.88, 154.51, 170.30.

2-(2-Butoxyethoxy)ethyl 4-methylbenzenesulfonate (21):

To a 0 °C solution of diethylene glycol butyl ether (16.22 g, 0.10 mole) and NaOH (6.0 g, 0.15 mole) in THF (200 mL) and H_2O (40 mL), TsCl (21.0 g, 0.11 mole dissolved in 60 mL of THF) was added dropwise (the temperature was maintained below 5 °C). After complete addition, the reaction mixture was stirred at 0 °C for 3 hours. The reaction mixture was poured into cold water (100 mL) and extracted with CH_2Cl_2. The CH_2Cl_2 extract was washed by H_2O (pH = 1) and brine then dried over $MgSO_4$ and filtered. The solvent was removed in a rotatory evaporator and passed through a short column of silica gel using (EtOAc/Hexane = 3/7) as eluent to give 27.0 g (85 %) as colorless oil. TLC (EtOAc/Hexane = 3/7): R_f = 0.58; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.91 (t, 3H, C*H*$_3$, *J* = 7.17), 1.34 (m, 2H, CH_3C*H*$_2$), 1.53 (m, 2H, CH_3CH_2C*H*$_2$), 2.44 (s, 3H, PhC*H*$_3$), 3.42 (m, 2H, $CH_3CH_2CH_2$C*H*$_2$), 3.51 (m, 2H, $CH_3CH_2CH_2CH_2$OC*H*$_2$), 3.57 (m, 2H, $CH_3CH_2CH_2CH_2OCH_2$C*H*$_2$), 3.69 (m, 2H, C*H*$_2$CH$_2$OTs), 4.16 (m, 2H, C*H*$_2$OTs), 7.34 (d, 2H, Ar*H*, *ortho* to CH_3, *J* = 7.93 Hz), 7.80 (d, 2H, Ar*H*, *meta* to CH_3, *J* = 7.93 Hz).

Methyl 3,4,5-tris(2-(2-butoxyethoxy)ethoxy)benzoate (22):

To a thoroughly degassed suspension of anhydrous K_2CO_3 (12.61 g, 0.091 mole) in DMF (60 mL) was added methyl gallate (2.80 g, 0.015 mole) and the reaction mixture was

heated to 70 °C which was added compound **21** (14.43 g, 0.046 mole) under N_2 atmosphere. After stirring for 6 h at 70 °C, the reaction mixture was poured into ice-cooled water and extracted with CH_2Cl_2. The CH_2Cl_2 extract was washed by H_2O, HCl (1 M) and brine then dried over $MgSO_4$ and filtered. The solvent was removed in a rotatory evaporator and passed through a short column of basic Al_2O_3 using CH_2Cl_2 as eluent to give 8.9 g (95 %) as pale-yellow oil. TLC (EtOAc/hexane = 3/7): R_f = 0.30; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.89 (t, 9H, C*H*$_3$, *J* = 7.48), 1.35 (m, 6H, CH_3CH_2), 1.55 (m, 6H, $CH_3CH_2CH_2$), 3.45 (m, 6H, $CH_3CH_2CH_2CH_2$), 3.58 (m, 6H, $CH_3CH_2CH_2CH_2OCH_2$), 3.70 (m, 6H, $CH_3CH_2CH_2CH_2OCH_2CH_2$), 3.80 (t, 2H, OCH_2CH_2 *para* to CO_2CH_3, *J* = 5.04 Hz), 3.87 (overlapped m, 7H, OCH_2CH_2 *meta* to CO_2CH_3, CO_2CH_3), 4.18 (t, 4H, OCH_2 *meta* to CO_2CH_3, *J* = 5.04 Hz), 4.25 (t, 2H, OCH_2 *para* to CO_2CH_3, *J* = 5.04 Hz), 7.29 (s, 2H, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 13.81, 19.17, 31.62, 52.02, 68.83, 69.57, 70.10, 70.52, 70.83, 71.21, 72.40, 108.97, 124.93, 142.59, 152.32, 166.65.

3,4,5-Tris(2-(2-butoxyethoxy)ethoxy)benzoic acid (23):

Compound **22** (4.0 g, 0.0065 mole), EtOH (40 mL, 95%), and KOH (2.2 g, 0.039 mole) were placed into a 100 mL round-bottom flask containing a Teflon coated magnetic stirring bar and heated to reflux for 2 h under constant stirring. After the reaction was completed it was cooled to room temperature and diluted with THF (20 mL). The solution was acidified with glacial CH_3COOH to pH 3. The reaction mixture was poured into ice-cooled water and extracted with CH_2Cl_2. The CH_2Cl_2 extract was washed by H_2O and brine then dried over $MgSO_4$ and filtered. The solvent was removed in a rotatory evaporator to yield 3.8 g (97 %) of viscous red oil. TLC (EtOAc/hexane = 3/7): R_f =

0.05; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.91 (t, 3H, C*H*$_3$, *J* = 7.32 Hz), 1.35 (m, 2H, CH_3CH_2), 1.54 (m, 2H, $CH_3CH_2CH_2$), 3.46 (m, 2H, $CH_3CH_2CH_2CH_2$), 3.59 (m, 2H, $CH_3CH_2CH_2CH_2OCH_2$), 3.72 (m, 2H, $CH_3CH_2CH_2CH_2OCH_2CH_2$), 3.82 (t, 2H, OCH_2CH_2 *para* to CO_2H, *J* = 4.73 Hz), 3.88 (t, 4H, OCH_2CH_2 *meta* to CO_2H, *J* = 4.73 Hz), 4.21 (t, 4H, OCH_2 *meta* to CO_2H, *J* = 4.73 Hz), 4.25 (t, 2H, OCH_2 *para* to CO_2H, *J* = 4.73 Hz), 7.35 (s, 2H, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 13.83, 19.18, 31.60, 68.82, 69.58, 70.10, 70.52, 70.82, 71.24, 72.43, 109.43, 124.26, 143.09, 152.33, 170.44.

(3,4,5-Tris(octyloxy)phenyl)methanol (24):

To a stirred suspension of $LiAlH_4$ (0.33 g, 0.0086 mole) in dry THF (20 mL) at 0 °C was added slowly compound **8** (3.0 g, 0.0058 mole dissolved in 5 mL dry THF) under N_2 atmosphere. After complete addition, the reaction mixture was allowed to warm to room temperature and stirred for 2 hours, after which TLC showed completion. The reaction was quenched by successive addition of H_2O (0.5 mL), 15% aq. NaOH (0.5 mL), and H_2O (1.5 mL) with continuous stirring until H_2 evolution ceased. The reaction mixture was filtered, and the lithium salt was washed with CH_2Cl_2. The filtrate was dried over $MgSO_4$ and the solvent was removed in a rotary evaporator to yield 2.6 g (93 %). TLC (EtOAc/hexane = 1/9): R_f = 0.11; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.89 (t, 9H, C*H*$_3$, *J* = 6.40 Hz), 1.31 (overlapped m, 24H, $CH_3(CH_2)_4$), 1.47 (m, 6H, $CH_2(CH_2)_2O$), 1.70 (br s, 1H, O*H*), 1.78 (m, 6H, CH_2CH_2O), 3.96 (overlapped t, 6H, OCH_2), 4.60 (s, 2H, $PhCH_2OH$), 6.56 (s, 2H, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.31, 22.87, 26.31, 29.61, 29.72, 30.46, 32.09, 65.89, 69.34, 73.57, 105.53, 136.21, 137.67, 153.49.

(3,4,5-Tris(dodecyloxy)phenyl)methanol (25):

To a stirred suspension of $LiAlH_4$ (0.25 g, 0.0065 mole) in dry THF (15 mL) at 0 °C was added slowly compound **9** (3.0 g, 0.0044 mole dissolved in 10 mL dry THF) under N_2 atmosphere. After complete addition, the reaction mixture was allowed to warm to room temperature and stirred for 2 hours, after which TLC showed completion. The reaction was quenched by successive addition of H_2O (0.5 mL), 15% aq. NaOH (0.75 mL), and H_2O (1.5 mL) with continuous stirring until H_2 evolution ceased. The reaction mixture was filtered, and the lithium salt was washed with CH_2Cl_2. The filtrate was dried over $MgSO_4$ and the solvent was removed in a rotary evaporator to yield 2.73 g (95 %). TLC (EtOAc/hexane = 1/9): R_f = 0.17; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.89 (t, 9H, C*H*$_3$, *J* = 7.02 Hz), 1.28 (overlapped m, 48H, $CH_3(CH_2)_8$), 1.46 (m, 6H, C*H*$_2$$(CH_2)_2O$), 1.61 (br t, 1H, O*H*, *J* = 5.80 Hz), 1.78 (m, 6H, C*H*$_2$$CH_2O$), 3.94 (t, 2H, OC*H*$_2$ *para* to CH_2OH, *J* = 6.56 Hz), 3.98 (t, 4H, OC*H*$_2$ *meta* to CH_2OH, *J* = 6.56 Hz), 4.60 (d, 2H, PhC*H*$_2$OH, *J* = 5.49 Hz), 6.57 (s, 2H, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.03, 22.58, 26.11, 29.37, 29.62, 30.26, 31.91, 65.39, 69.04, 73.37, 105.13, 136.22, 137.47, 153.10.

(3,4,5-Tris(2-(2-methoxyethoxy)ethoxy)phenyl)methanol (26):

To a stirred suspension of $LiAlH_4$ (0.40 g, 0.0105 mole) in dry THF (20 mL) at 0 °C was added slowly compound **19** (3.43 g, 0.007 mole dissolved in 10 mL dry THF) under N_2 atmosphere. After complete addition, the reaction mixture was allowed to warm to room temperature and stirred for 2 hours, after which TLC showed completion. The reaction was quenched by successive addition of H_2O (0.7 mL), 15% aq. NaOH (0.7 mL), and

H_2O (2.1 mL) with continuous stirring until H_2 evolution ceased. The reaction mixture was filtered, and the lithium salt was washed with CH_2Cl_2. The filtrate was dried over $MgSO_4$ and the solvent was removed in a rotary evaporator to yield 2.6 g (81 %) of viscous yellow oil. TLC (EtOAc/hexane = 7/3): R_f = 0.11; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.26 (br s, 1H, O*H*), 3.36 (s, 9H, C*H*$_3$), 3.54 (m, 6H, CH_3OCH_2), 3.70 (m, 6H, $CH_3OCH_2CH_2$), 3.79 (t, 2H, OCH_2CH_2 *para* to CH_2OH, *J* = 5.04 Hz), 3.83 (t, 4H, OCH_2CH_2 *meta* to CH_2OH, *J* = 4.88 Hz), 4.14 (m, 6H, OCH_2), 4.55 (s, 2H, $PhCH_2OH$), 6.59 (s, 2H, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 58.92, 65.06, 68.67, 69.71, 70.29, 70.44, 70.57, 71.89, 71.94, 72.26, 106.23, 136.71, 137.51, 152.62.

(3,4,5-Tris(2-(2-butoxyethoxy)ethoxy)phenyl)methanol (27):

To a stirred suspension of $LiAlH_4$ (0.42 g, 0.0112 mole) in dry THF (20 mL) at 0 °C was added slowly compound **22** (4.60 g, 0.0075 mole dissolved in 10 mL dry THF) under N_2 atmosphere. After complete addition, the reaction mixture was allowed to warm to room temperature and stirred for 2 hours, after which TLC showed completion. The reaction was quenched by successive addition of H_2O (0.75 mL), 15% aq. NaOH (0.75 mL), and H_2O (2.25 mL) with continuous stirring until H_2 evolution ceased. The reaction mixture was filtered, and the lithium salt was washed with CH_2Cl_2. The filtrate was dried over $MgSO_4$ and the solvent was removed in a rotary evaporator to yield 4.1 g (93 %) of viscous yellow oil. TLC (EtOAc/hexane = 5/5): R_f = 0.20; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.88 (t, 9H, C*H*$_3$, *J* = 7.40 Hz), 1.33 (m, 6H, CH_3CH_2), 1.53 (m, 6H, $CH_3CH_2CH_2$), 1.82 (s, 1H, O*H*), 3.43 (t, 6H, $CH_3CH_2CH_2CH_2$, *J* = 6.71 Hz), 3.56 (dd, 6H, $CH_3CH_2CH_2CH_2OCH_2$, *J* = 5.49 Hz), 3.68 (m, 6H, $CH_3CH_2CH_2CH_2OCH_2CH_2$),

3.77 (t, 2H, OCH_2CH_2 *para* to CH_2OH, J = 5.19 Hz), 3.81 (t, 4H, OCH_2CH_2 *meta* to CH_2OH, J = 5.04 Hz), 4.11 (m, 6H, OCH_2), 4.53 (s, 2H, $PhCH_2OH$), 6.57 (s, 2H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 13.74, 19.09, 31.53, 64.91, 68.71, 69.66, 70.02, 70.39, 70.68, 71.10, 72.21, 106.25, 136.74, 137.55, 152.61.

5-(Chloromethyl)-1,2,3-tris(octyloxy)benzene (28):

A two-neck round bottom flask equipped with a Teflon-coated magnetic stirrer and an addition funnel was charged with compound **24** (1.48 g, 0.003 mole) in dry CH_2Cl_2 (15 mL) and catalytic amount of DMF. The reaction flask was flushed with N_2, and cooled in an ice bath at 0°C. Thionyl chloride (0.26 mL, 0.0036 mole dissolved in 10 mL dry CH_2Cl_2) was added dropwise to the cooled reaction mixture. After complete addition, the reaction mixture was stirred at room temperature for 30 min. The solvent was removed in a rotary evaporator and the residue was recrystallized from acetone to yield 1.5 g (98 %). TLC (EtOAc/hexane = 1/9): R_f = 0.85; ^1H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.89 (t, 9H, CH_3, J = 6.40 Hz), 1.31 (overlapped m, 24H, $CH_3(CH_2)_4$), 1.47 (m, 6H, $CH_2(CH_2)_2O$), 1.78 (m, 6H, CH_2CH_2O), 3.96 (overlapped t, 6H, OCH_2), 4.52 (s, 2H, $PhCH_2Cl$), 6.57 (s, 2H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.32, 22.79, 26.41, 29.51, 29.82, 30.56, 32.19, 65.82, 69.41, 73.67, 105.43, 136.31, 137.78, 153.69.

5-(Chloromethyl)-1,2,3-tris(dodecyloxy)benzene (29):

A two-neck round bottom flask equipped with a Teflon-coated magnetic stirrer and an addition funnel was charged with compound **25** (1.5 g, 0.0023 mole) in dry CH_2Cl_2 (15 mL) and catalytic amount of DMF. The reaction flask was flushed with N_2, and cooled in

an ice bath at 0°C. Thionyl chloride (0.2 mL, 0.0027 mole dissolved in 10 mL dry CH_2Cl_2) was added dropwise to the cooled reaction mixture. After complete addition, the reaction mixture was stirred at room temperature for 30 min. The solvent was removed in a rotary evaporator and the residue was recrystallized from acetone to yield 1.5 g (98 %). TLC (EtOAc/hexane = 1/9): R_f = 0.76; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.89 (t, 9H, C*H*$_3$, *J* = 6.90 Hz), 1.31 (overlapped m, 48H, $CH_3(CH_2)_8$), 1.47 (m, 6H, $CH_2(CH_2)_2O$), 1.78 (m, 6H, CH_2CH_2O), 3.97 (overlapped t, 6H, OCH_2), 4.52 (s, 2H, $PhCH_2Cl$), 6.58 (s, 2H, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.13, 22.68, 26.21, 29.47, 29.72, 30.36, 31.81, 65.49, 69.14, 73.47, 105.23, 136.32, 137.57, 153.40.

5-(Chloromethyl)-1,2,3-tris(2-(2-methoxyethoxy)ethoxy)benzene (30):

A two-neck round bottom flask equipped with a Teflon-coated magnetic stirrer and an addition funnel was charged with compound **26** (2.54 g, 0.0055 mole) and DTBMP (1.69 g, 0.0083 mole) in dry CH_2Cl_2 (30 mL). The reaction flask was flushed with N_2, and cooled in an ice bath at 0°C. Thionyl chloride (0.44 mL, 0.0061 mole dissolved in 10 mL dry CH_2Cl_2) was added dropwise to the cooled reaction mixture. After complete addition, the reaction mixture was stirred at room temperature for 30 min. The solvent was removed in a rotary evaporator to yield 2.5 g (94 %). TLC (EtOAc/hexane = 1/9): R_f = 0.90. The product was used in next reaction without further purification.

1,2,3-Tris(2-(2-butoxyethoxy)ethoxy)-5-(chloromethyl)benzene (31):

A two-neck round bottom flask equipped with a Teflon-coated magnetic stirrer and an addition funnel was charged with compound **27** (3.90 g, 0.0066 mole) and DTBMP (2.04

g, 0.0099 mole) in dry CH_2Cl_2 (30 mL). The reaction flask was flushed with N_2, and cooled in an ice bath at 0°C. Thionyl chloride (0.53 mL, 0.0073 mole dissolved in 10 mL dry CH_2Cl_2) was added dropwise to the cooled reaction mixture. After complete addition, the reaction mixture was stirred at room temperature for 30 min. The solvent was removed in a rotary evaporator to yield 3.9 g (97 %). TLC (EtOAc/hexane = 1/9): Rf = 0.80. The product was used in next reaction without further purification.

Methyl 3,4,5-tris(3,4,5-tris(octyloxy)benzyloxy)benzoate (32):

To a thoroughly degassed suspension of anhydrous K_2CO_3 (1.08 g, 0.0078 mole) in DMF (20 mL) was added methyl gallate (0.24 g, 0.0013 mole) and the reaction mixture was heated to 70 °C which was added compound **28** (2.0 g, 0.0039 mole) under N_2 atmosphere. After stirring for 8 h at 70 °C, the reaction mixture was poured into ice-cooled water and the precipitate was collected by filtration and vacuum dried. The crude product was passed through a short column of basic Al_2O_3 using CH_2Cl_2 as eluent followed by recrystallization from acetone to yield 1.6 g (76 %). TLC (EtOAc/hexane = 1/9): R_f = 0.40; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.88 (t, 27H, C*H*$_3$, *J* = 6.40 Hz), 1.29 (overlapped m, 72H, $CH_3(CH_2)_4$), 1.43 (m, 18H, C*H*$_2$$(CH_2)_2O$), 1.74 (m, 18H, C*H*$_2$$CH_2O$), 3.76 (t, 4H, OC*H*$_2$, 4-(3',5') positions, *J* = 6.40 Hz), 3.89 (m, 11H, OC*H*$_2$, 3,5-(3',5') positions, CO_2CH_3), 3.93 (t, 6H, OC*H*$_2$, 3,4,5-(4') positions, *J* = 6.50 Hz), 5.04 (s, 6H, PhC*H*$_2$), 6.62 (s, 2H, Ar*H*, *ortho* to $PhOCH_2$, 4' position), 6.64 (s, 4H, Ar*H*, *ortho* to $PhOCH_2$, 3',5' positions), 7.38 (s, 2H, Ar*H*, *ortho* to CO_2CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.31, 22.88, 26.41, 29.59, 29.77, 30.61, 32.09, 52.43, 69.22, 71.75, 73.51, 75.42, 105.91, 106.42, 109.78, 125.44, 131.93, 132.63, 137.96, 142.71, 152.79, 153.21, 153.54, 166.78.

Methyl 3,4,5-tris(3,4,5-tris(dodecyloxy)benzyloxy)benzoate (33):

To a thoroughly degassed suspension of anhydrous K_2CO_3 (0.61 g, 044 mole) in DMF (20 mL) was added methyl gallate (0.14 g, 0.00074 mole) and the reaction mixture was heated to 70 °C which was added compound **29** (1.5 g, 0.0022 mole) under N_2 atmosphere. After stirring for 8 h at 70 °C, the reaction mixture was poured into ice-cooled water and the precipitate was collected by filtration and vacuum dried. The crude product was passed through a short column of basic Al_2O_3 using CH_2Cl_2 as eluent followed by recrystallization from acetone to yield 1.33 g (88 %). TLC (EtOAc/hexane = 1/9): R_f = 0.60; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.88 (t, 27H, C*H*$_3$, *J* = 7.60 Hz), 1.27 (overlapped m, 144H, $CH_3(CH_2)_8$), 1.44 (m, 18H, C*H*$_2$$(CH_2)_2O$), 1.73 (m, 18H, C*H*$_2$$CH_2O$), 3.76 (t, 4H, OC*H*$_2$, 4-(3',5') positions, *J* = 5.80 Hz), 3.89 (m, 11H, OC*H*$_2$, 3,5-(3',5') positions, CO_2CH_3), 3.93 (t, 6H, OC*H*$_2$, 3,4,5-(4') positions, *J* = 7.60 Hz), 5.04 (s, 6H, PhC*H*$_2$), 6.61 (s, 2H, Ar*H*, *ortho* to $PhOCH_2$, 4' position), 6.64 (s, 4H, Ar*H*, *ortho* to $PhOCH_2$, 3',5' positions), 7.38 (s, 2H, Ar*H*, *ortho* to CO_2CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.11, 22.68, 26.21, 29.39, 29.67, 30.41, 31.88, 52.23, 69.12, 71.65, 73.41, 75.12, 105.68, 106.22, 109.58, 125.14, 131.73, 132.43, 137.76, 142.11, 152.49, 153.01, 153.34, 166.48.

Methyl 3,4,5-tris(3,4,5-tris(2-(2-methoxyethoxy)ethoxy)benzyloxy)benzoate (34):

To a thoroughly degassed suspension of anhydrous K_2CO_3 (1.20 g, 0.0087 mole) in DMF (25 mL) was added methyl gallate (0.32 g, 0.0017 mole) and the reaction mixture was heated to 70 °C which was added compound **30** (2.50 g, 0.0052 mole) under N_2 atmosphere. After stirring for 8 h at 70 °C, the reaction mixture was poured into ice-

cooled water and extracted with CH_2Cl_2. The CH_2Cl_2 extract was washed by H_2O and brine then dried over $MgSO_4$ and filtered. The solvent was removed in a rotatory evaporator and passed through a short column of basic Al_2O_3 using CH_2Cl_2 as eluent. Purification by column chromatography ($MeOH/CH_2Cl_2$ = 0-1 %) yielded 1.6 g (61 %) as viscous red oil. TLC ($MeOH/CH_2Cl_2$ = 5 %): R_f = 0.53; ^1H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 3.35 (m, 27H, C*H*$_3$), 3.53 (m, 18H, CH_3OCH_2), 3.68 (m, 18H, $CH_3OCH_2CH_2$), 3.79 (m, 18H, OCH_2CH_2), 3.86 (s, 3H, CO_2CH_3), 3.96 (t, 4H, OCH_2, 4-(3',5') positions, *J* = 4.88 Hz), 4.09 (overlapped t, 10H, OCH_2, 3,5-(3',5') positions, 4-(4') position), 4.15 (t, 4H, OCH_2, 3,5-(4') positions, *J* = 5.04 Hz), 5.02 (s, 6H, $PhCH_2$), 6.63 (s, 2H, Ar*H*, *ortho* to $PhOCH_2$, 4' position), 6.65 (s, 4H, Ar*H*, *ortho* to $PhOCH_2$, 3',5' positions), 7.32 (s, 2H, Ar*H*, *ortho* to CO_2CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 52.13, 58.91, 68.52, 68.69, 69.60, 70.30, 70.51, 70.58, 71.29, 71.86, 71.95, 72.27, 72.32, 74.77, 106.56, 107.03, 109.53, 125.25, 132.11, 132.91, 137.77, 137.89, 142.23, 152.36, 152.41, 152.73, 166.44.

Methyl 3,4,5-tris(3,4,5-tris(2-(2-butoxyethoxy)ethoxy)benzyloxy)benzoate (35):

To a thoroughly degassed suspension of anhydrous K_2CO_3 (1.44 g, 0.01 mole) in DMF (30 mL) was added methyl gallate (0.38 g, 0.002 mole) and the reaction mixture was heated to 70 °C which was added compound **31** (3.80 g, 0.006 mole) under N_2 atmosphere. After stirring for 8 h at 70 °C, the reaction mixture was poured into ice-cooled water and extracted with CH_2Cl_2. The CH_2Cl_2 extract was washed by H_2O and brine then dried over $MgSO_4$ and filtered. The solvent was removed in a rotatory evaporator and passed through a short column of basic Al_2O_3 using CH_2Cl_2 as eluent. Purification by column chromatography (EtOAc/hexane = 6/4) yielded 2.4 g 618 %) as

viscous red oil. TLC (EtOAc/hexane = 7/3): R_f = 0.68; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.91 (t, 27H, C*H*$_3$, *J* = 7.40 Hz), 1.33 (m, 18H, CH_3CH_2), 1.56 (m, 18H, $CH_3CH_2CH_2$), 3.45 (m, 18H, $CH_3CH_2CH_2CH_2$), 3.58 (m, 18H, $CH_3CH_2CH_2CH_2OCH_2$), 3.70 (m, 18H, $CH_3CH_2CH_2CH_2OCH_2CH_2$), 3.82 (m, 18H, OCH_2CH_2), 3.88 (s, 3H, CO_2CH_3), 3.96 (t, 4H, OCH_2, 4-(3',5') positions, *J* = 4.88 Hz), 4.09 (overlapped t, 10H, OCH_2, 3,5-(3',5') positions, 4-(4') position), 4.15 (t, 4H, OCH_2, 3,5-(4') positions, *J* = 5.04 Hz), 5.02 (s, 4H, $PhCH_2$ *meta* to CO_2CH_3), 5.04 (s, 2H, $PhCH_2$ *para* to CO_2CH_3), 6.64 (s, 2H, Ar*H*, *ortho* to $PhOCH_2$, 4' position), 6.66 (s, 4H, Ar*H*, *ortho* to $PhOCH_2$, 3',5' positions), 7.33 (s, 2H, Ar*H*, *ortho* to CO_2CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 13.74, 19.09, 31.53, 52.13, 68.52, 68.69, 69.60, 70.30, 70.51, 70.58, 71.29, 71.86, 71.95, 72.27, 72.32, 74.77, 106.56, 107.03, 109.53, 125.25, 132.11, 132.91, 137.77, 137.89, 142.23, 152.36, 152.41, 152.73, 166.44.

3,4,5-Tris(3,4,5-tris(octyloxy)benzyloxy)benzoic acid (36):

Compound **32** (1.20 g, 0.00075 mole), EtOH (20 mL, 95%), and KOH (0.25 g, 0.0045 mole) were placed into a round-bottom flask containing a Teflon coated magnetic stirring bar and heated to reflux for 2 h under constant stirring. After the reaction was completed it was cooled to room temperature and diluted with THF (40 mL). The solution was acidified with glacial CH_3COOH to pH 3. The reaction mixture was poured into ice-cooled water and stirred for 15 min. The precipitate was collected and dried. The solid was dissolved in minimum volume of CH_2Cl_2 and precipitated in cold MeOH to yield 1.13 g (95 %). TLC (EtOAc/hexane = 1/9): R_f = 0.05; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.88 (t, 27H, C*H*$_3$, *J* = 6.40 Hz), 1.28 (overlapped m, 72H, $CH_3(CH_2)_4$), 1.43 (m, 18H, $CH_2(CH_2)_2O$), 1.73 (m, 18H, CH_2CH_2O), 3.76 (t, 4H, OCH_2, 4-(3',5') positions,

J = 6.40 Hz), 3.89 (m, 8H, OC*H*$_2$, 3,5-(3',5') positions, *J* = 6.40 Hz), 3.94 (t, 6H, OC*H*$_2$, 3,4,5-(4') positions, *J* = 6.50 Hz), 5.05 (s, 6H, PhC*H*$_2$), 6.62 (s, 2H, Ar*H*, *ortho* to PhOCH$_2$, 4' position), 6.64 (s, 4H, Ar*H*, *ortho* to PhOCH$_2$, 3',5' positions), 7.46 (s, 2H, Ar*H*, *ortho* to CO_2H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.31, 22.88, 26.41, 29.59, 29.77, 30.61, 32.09, 69.12, 71.85, 73.51, 75.42, 105.91, 106.42, 110.28, 124.41, 131.73, 132.53, 137.98, 143.51, 152.80, 153.24, 153.54, 171.58.

3,4,5-Tris(3,4,5-tris(dodecyloxy)benzyloxy)benzoic acid (37):

Compound **33** (0.79 g, 0.00052 mole), EtOH (20 mL, 95%), and KOH (0.18 g, 0.00312 mole) were placed into a round-bottom flask containing a Teflon coated magnetic stirring bar and heated to reflux for 2 h under constant stirring. After the reaction was completed it was cooled to room temperature and diluted with THF (40 mL). The solution was acidified with glacial CH_3COOH to pH 3. The reaction mixture was poured into ice-cooled water and stirred for 15 min. The precipitate was collected and dried. The solid was dissolved in minimum volume of CH_2Cl_2 and precipitated in cold MeOH to yield 1.05 g (96 %). TLC (EtOAc/hexane = 1/9): R_f = 0.10; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.89 (t, 27H, C*H*$_3$, *J* = 7.60 Hz), 1.27 (overlapped m, 144H, $CH_3(CH_2)_8$), 1.44 (m, 18H, C*H*$_2$(CH$_2$)$_2$O), 1.74 (m, 18H, C*H*$_2$CH$_2$O), 3.76 (t, 4H, OC*H*$_2$, 4-(3',5') positions, *J* = 7.00 Hz), 3.90 (t, 8H, OC*H*$_2$, 3,5-(3',5') positions, *J* = 6.10 Hz), 3.94 (t, 6H, OC*H*$_2$, 3,4,5-(4') positions, *J* = 6.40 Hz), 5.05 (s, 6H, PhC*H*$_2$), 6.61 (s, 2H, Ar*H*, *ortho* to PhOCH$_2$, 4' position), 6.65 (s, 4H, Ar*H*, *ortho* to PhOCH$_2$, 3',5' positions), 7.46 (s, 2H, Ar*H*, *ortho* to CO_2H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.13, 22.68, 26.21, 29.37, 29.72, 30.41, 31.88, 69.14, 71.71, 73.35, 75.23, 105.81, 106.24, 110.08, 124.21, 131.49, 132.32, 137.91, 143.37, 152.61, 153.01, 153.32, 171.54.

3,4,5-Tris(3,4,5-tris(2-(2-methoxyethoxy)ethoxy)benzyloxy)benzoic acid (38):

Compound **34** (0.79 g, 0.00052 mole), EtOH (20 mL, 95%), and KOH (0.17 g, 0.00311 mole) were placed into a 50 mL round-bottom flask containing a Teflon coated magnetic stirring bar and heated to reflux for 2 h under constant stirring. After the reaction was completed it was cooled to room temperature and diluted with THF (10 mL). The solution was acidified with glacial CH_3COOH to pH 3. The reaction mixture was poured into ice-cooled water and extracted with CH_2Cl_2. The CH_2Cl_2 extract was washed by H_2O and brine then dried over $MgSO_4$ and filtered. The solvent was removed in a rotatory evaporator to yield 0.70 g (90 %) of viscous red oil. TLC ($MeOH/CH_2Cl_2$ = 5 %): R_f = 0.05; ^1H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 3.38 (m, 27H, C*H*$_3$), 3.55 (m, 18H, CH_3OCH_2), 3.70 (m, 18H, $CH_3OCH_2CH_2$), 3.81 (m, 18H, OCH_2CH_2), 4.03 (t, 4H, OC*H*$_2$, 4-(3',5') positions, *J* = 4.88 Hz), 4.13 (overlapped t, 14H, OC*H*$_2$, 3,5-(3',5') positions, 3,4,5-(4') positions), 5.03 (s, 4H, PhC*H*$_2$ *meta* to CO_2H), 5.04 (s, 2H, PhC*H*$_2$ *ortho* to CO_2H), 6.67 (s, 4H, Ar*H*, *ortho* to $PhrOCH_2$, 3',5' positions), 6.68 (s, 2H, Ar*H*, *ortho* to $PhOCH_2$, 4' positions), 7.35 (s, 2H, Ar*H*, *ortho* to CO_2H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 58.96, 68.64, 68.76, 69.56, 69.64, 70.36, 70.54, 70.60, 71.52, 71.94, 71.99, 72.02, 72.36, 74.89, 107.10, 107.29, 109.19, 110.30, 125.09, 132.24, 133.00, 137.94, 138.09, 142.45, 152.29, 152.51, 152.78, 167.58.

3,4,5-Tris(3,4,5-tris(2-(2-butoxyethoxy)ethoxy)benzyloxy)benzoic acid (39):

Compound **35** (1.75 g, 0.0093 mole), EtOH (25 mL, 95%), and KOH (0.32 g, 0.0056 mole) were placed into a 50 mL round-bottom flask containing a Teflon coated magnetic stirring bar and heated to reflux for 2 h under constant stirring. After the reaction was

completed it was cooled to room temperature and diluted with THF (10 mL). The solution was acidified with glacial CH_3COOH to pH 3. The reaction mixture was poured into ice-cooled water and extracted with CH_2Cl_2. The CH_2Cl_2 extract was washed by H_2O and brine then dried over $MgSO_4$ and filtered. The solvent was removed in a rotatory evaporator to yield 1.6 g (94 %) of viscous red oil. TLC (EtOAc/hexane = 7/3): R_f = 0.05; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.91 (t, 27H, C*H*$_3$, *J* = 7.40 Hz), 1.33 (m, 18H, CH_3CH_2), 1.56 (m, 18H, $CH_3CH_2CH_2$), 3.45 (m, 18H, $CH_3CH_2CH_2CH_2$), 3.58 (m, 18H, $CH_3CH_2CH_2CH_2OCH_2$), 3.70 (m, 18H, $CH_3CH_2CH_2CH_2OCH_2CH_2$), 3.82 (m, 18H, OCH_2CH_2), 3.96 (t, 4H, OCH_2, 4-(3',5') positions, *J* = 4.88 Hz), 4.09 (overlapped t, 10H, OCH_2, 3,5-(3',5') positions, 4-(4') position), 4.15 (t, 4H, OCH_2, 3,5-(4') positions, *J* = 5.04 Hz), 5.02 (s, 4H, PhCH_2 *meta* to CO_2H), 5.04 (s, 2H, PhCH_2 *para* to CO_2H), 6.64 (s, 2H, Ar*H*, *ortho* to $PhOCH_2$, 4' position), 6.66 (s, 4H, Ar*H*, *ortho* to $PhOCH_2$, 3',5' positions), 7.33 (s, 2H, Ar*H*, *ortho* to CO_2H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 13.74, 19.09, 31.53, 68.52, 68.69, 69.60, 70.30, 70.51, 70.58, 71.29, 71.86, 71.95, 72.27, 72.32, 74.77, 107.56, 108.03, 110.53, 125.25, 132.11, 133.91, 138.77, 137.89, 143.23, 153.36, 152.41, 153.73, 167.44.

1,2,3-Tris(octyloxy)benzene (40):

To a thoroughly degassed suspension of anhydrous K_2CO_3 (24.9 g, 0.18 mole) in DMF (100 mL) was added pyrogallol (3.8 g, 0.03 mole) and the reaction mixture was heated to 80 °C which was added 1-bromooctane (23.2 g, 0.12 mole) under N_2 atmosphere. After stirring for 8 h at 80 °C, the reaction mixture was poured into ice-cooled water and extracted with CH_2Cl_2. The CH_2Cl_2 extract was washed by H_2O and brine then dried over $MgSO_4$ and filtered. The solvent was removed in a rotatory evaporator and passed

through a short column of basic Al_2O_3 using CH_2Cl_2 as eluent to give 13.2 g (95 %) as colorless oil. TLC (EtOAc/hexane = 1/9): R_f = 0.80; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.91 (t, 9H, C*H*$_3$, *J* = 6.71 Hz), 1.33 (overlapped m, 24H, $CH_3(CH_2)_4$), 1.49 (m, 6H, C*H*$_2$$(CH_2)_2O$), 1.80 (m, 6H, C*H*$_2$$CH_2O$), 3.98 (m, 6H, C*H*$_2$O), 6.56 (d, 2H, Ar*H*, 4,6 positions, *J* = 8.24 Hz), 6.92 (t, 1H, Ar*H*, 5 position, *J* = 8.39 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.31, 22.93, 26.12-30.18, 32.21, 69.41, 73.62, 107.21, 123.29, 138.54, 153.71.

1,2,3-Tris(dodecyloxy)benzene (41):

To a thoroughly degassed suspension of anhydrous K_2CO_3 (69.1 g, 0.5 mole) in DMF (160 mL) was added pyrogallol (12.6 g, 0.1 mole) and the reaction mixture was heated to 80 °C which was added 1-bromododecane (74.8 g, 0.3 mole) under N_2 atmosphere. After stirring for 8 hours at 80 °C, the reaction mixture was poured into ice-cooled water and the precipitate was collected by filtration and vacuum dried. Recrystallization from *iso*-propanol yielded 47.3 g (75 %). TLC (EtOAc/hexane = 1/9): R_f = 0.79; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.89 (t, 9H, C*H*$_3$, *J* = 7.02 Hz), 1.28 (overlapped m, 48H, $CH_3(CH_2)_8$), 1.48 (m, 6H, C*H*$_2$$(CH_2)_2O$), 1.78 (m, 6H, C*H*$_2$$CH_2O$), 3.97 (m, 6H, C*H*$_2$O), 6.55 (d, 2H, Ar*H*, 4,6 positions, *J* = 8.24 Hz), 6.91 (t, 1H, Ar*H*, 5 position, *J* = 8.39 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.31, 22.93, 26.12-30.18, 32.21, 69.41, 73.62, 107.21, 123.29, 138.54, 153.71.

5-Nitro-1,2,3-tris(octyloxy)benzene (42):

To a stirred suspension of $SiO_2 \cdot HNO_3$ (25.2 g, 0.08 mole, 20 % HNO3 w/w) in CH_2Cl_2 (130 mL) at room temperature, compound **40** (7.4 g, 0.016 mole dissolved in 20 mL

CH_2Cl_2) was added rapidly. The resulting red solution was stirred for 15 min, filtered and washed several times with CH_2Cl_2. The solution was concentrated in a rotary evaporator and precipitated in cold MeOH (100 mL). The yellow precipitate was collected by filtration and air-dried. Recrystallization from acetone yielded 5.7 g (70 %). TLC (EtOAc/hexane = 1/9): R_f = 0.76; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.89 (t, 9H, C*H*$_3$, *J* = 7.63 Hz), 1.31 (overlapped m, 24H, $CH_3(CH_2)_4$), 1.49 (m, 6H, $CH_2(CH_2)_2O$), 1.75 (m, 2H, CH_2CH_2O, 4 position), 1.84 (m, 4H, CH_2CH_2O, 3,5 positions), 4.05 (m, 6H, C*H*$_2$O), 7.47 (s, 2H, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.31, 22.93, 26.12-30.18, 32.11, 69.71, 73.95, 102.71, 143.39, 144.14, 152.91.

1,2,3-Tris(dodecyloxy)-5-nitrobenzene (43):

To a stirred suspension of $SiO_2 \cdot HNO_3$ (78.8 g, 0.25 mole, 20 % HNO3 w/w) in CH_2Cl_2 (400 mL) at room temperature, compound **41** (31.6 g, 0.05 mole dissolved in 100 mL CH_2Cl_2) was added rapidly. The resulting red solution was stirred for 15 min, filtered and washed several times with CH_2Cl_2. The solution was concentrated in a rotary evaporator and precipitated in cold MeOH (500 mL). The yellow precipitate was collected by filtration and air-dried. Recrystallization from *iso*-propanol yielded 26 g (77 %). TLC (EtOAc/hexane = 1/9): R_f = 0.73; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.89 (t, 9H, C*H*$_3$, *J* = 7.02 Hz), 1.28 (overlapped m, 48H, $CH_3(CH_2)_8$), 1.48 (m, 6H, $CH_2(CH_2)_2O$), 1.75 (m, 2H, CH_2CH_2O, 4 position), 1.84 (m, 4H, CH_2CH_2O, 3,5 positions), 4.05 (m, 6H, C*H*$_2$O), 7.48 (s, 2H, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.31, 22.93, 26.12-30.18, 32.11, 69.71, 73.95, 102.71, 143.39, 144.14, 152.91.

3,4,5-Tris(octyloxy)aniline (44):

A mixture of compound **42** (5.0 g, 0.01 mole), $NH_2NH_2 \cdot H_2O$ (1.50 g, 0.03 mole) and graphite (4.0 g) in EtOH (50 mL) was refluxed under N_2 atmosphere for 24 hours. The cooled mixture was diluted with CH_2Cl_2 (60 mL). Graphite was filtered and washed several times with CH_2Cl_2. The colorless solution was concentrated on a rotary evaporator and the resulting white solid was dissolved in CH_2Cl_2. After precipitation in MeOH, the obtained solid was collected by filtration and washed with cold MeOH. After drying under vacuum, 4.0 g (86 %) of a white powder was obtained. TLC (EtOAc/hexane = 1/9): R_f = 0.13; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.89 (t, 9H, C*H*$_3$, *J* = 7.32 Hz), 1.30 (overlapped m, 24H, $CH_3(CH_2)_4$), 1.45 (m, 6H, C*H*$_2$$(CH_2)_2O$), 1.76 (m, 6H, C*H*$_2$$CH_2O$), 3.47 (br s, 2H, N*H*$_2$), 3.85 (t, 2H, C*H*$_2$O, 4 position, *J* = 6.56 Hz), 3.91 (t, 4H, C*H*$_2$O, 3,5 positions, *J* = 6.41 Hz), 5.92 (s, 2H, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.51, 23.13, 26.12-30.18, 32.41, 69.51, 73.99, 95.01, 131.61, 142.68, 154.11.

3,4,5-Tris(dodecyloxy)aniline (45):

A mixture of compound **43** (2.14 g, 0.003 mole), $NH_2NH_2 \cdot H_2O$ (0.45 g, 0.009 mole) and graphite (1.5 g) in EtOH (20 mL) was refluxed under N_2 atmosphere for 24 hours. The cooled mixture was diluted with CH_2Cl_2 (25 mL). Graphite was filtered and washed several times with CH_2Cl_2. The colorless solution was concentrated on a rotary evaporator and the resulting white solid was dissolved in CH_2Cl_2. After precipitation in MeOH, the obtained solid was collected by filtration and washed with cold MeOH. After drying under vacuum, 1.75 g (91 %) of a white powder was obtained. TLC

(EtOAc/hexane = 1/9): R_f = 0.10; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.89 (t, 9H, C*H*$_3$, *J* = 7.02 Hz), 1.28 (overlapped m, 48H, $CH_3(CH_2)_8$), 1.45 (m, 6H, $CH_2(CH_2)_2O$), 1.75 (m, 6H, CH_2CH_2O), 3.86 (t, 2H, CH_2O, 4 position, *J* = 6.71 Hz), 3.92 (t, 4H, CH_2O, 3,5 positions, *J* = 6.41 Hz), 6.05 (s, 2H, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.51, 23.13, 26.12-30.18, 32.41, 69.51, 73.99, 95.01, 131.61, 142.68, 154.11.

1,2-Bis(octyloxy)benzene (46):

To a thoroughly degassed suspension of anhydrous K_2CO_3 (16.58 g, 0.12 mole) in DMF (100 mL) was added catechol (3.3 g, 0.03 mole) and the reaction mixture was heated to 80 °C which was added 1-bromooctane (17.4 g, 0.09 mole) under N_2 atmosphere. After stirring for 8 h at 80 °C, the reaction mixture was poured into ice-cooled water and the product was filtered and dried. The product was purified through a short column of basic Al_2O_3 using CH_2Cl_2 as eluent followed by recrystallization from acetone to give 8.5 g (85 %). TLC (EtOAc/hexane = 1/9): R_f = 0.70; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.89 (t, 6H, C*H*$_3$, *J* = 6.71 Hz), 1.31 (overlapped m, 16H, $CH_3(CH_2)_4$), 1.47 (m, 4H, $CH_2(CH_2)_2O$), 1.78 (m, 4H, CH_2CH_2O), 4.02 (m, 4H, CH_2O), 6.67 (dd, 2H, Ar*H*, 3,6 positions, *J* = 8.24 Hz), 6.92 (dd, 2H, Ar*H*, 4,5 position, *J* = 8.24 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.15, 22.73, 26.10-30.13, 32.07, 69.52, 122.21, 123.69, 152.41.

4-Nitro-1,2-bis(octyloxy)benzene (47):

To a stirred suspension of $SiO_2 \cdot HNO_3$ (40.0 g, 0.127 mole, 20 % HNO3 w/w) in CH_2Cl_2 (180 mL) at room temperature, compound **46** (8.5 g, 0.0254 mole dissolved in 20 mL

CH_2Cl_2) was added rapidly. The resulting red solution was stirred for 15 min, filtered and washed several times with CH_2Cl_2. The solution was concentrated in a rotary evaporator and precipitated in cold hexane (100 mL). The yellow precipitate was collected by filtration and air-dried. Recrystallization from acetone yielded 5.3 g (55 %). TLC (EtOAc/hexane = 1/9): R_f = 0.70; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.88 (t, 6H, C*H*$_3$, *J* = 6.71 Hz), 1.31 (overlapped m, 16H, $CH_3(CH_2)_4$), 1.46 (m, 4H, $CH_2(CH_2)_2O$), 1.77 (m, 4H, CH_2CH_2O), 4.03 (m, 4H, CH_2O), 7.12 (d, 1H, Ar*H*, meta to NO_2, *J* = 8.20 Hz), 7.68 (d, 1H, Ar*H*, *J* = 1.28 Hz), 7.74 (dd, 1H, Ar*H*, *J* = 8.20 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.11, 22.71, 26.13-30.15, 32.05, 69.43, 107.56, 117.21, 122.57, 140.45, 152.36, 155.71.

3,4-Bis(octyloxy)aniline (48):

A mixture of compound **47** (5.0 g, 0.013 mole), $NH_2NH_2{\cdot}H_2O$ (2.0 g, 0.039 mole) and graphite (4.0 g) in EtOH (50 mL) was refluxed under N_2 atmosphere for 24 hours. The cooled mixture was diluted with CH_2Cl_2 (60 mL). Graphite was filtered and washed several times with CH_2Cl_2. The colorless solution was concentrated on a rotary evaporator and the resulting white solid was dissolved in CH_2Cl_2. After precipitation in MeOH, the obtained solid was collected by filtration and washed with cold MeOH. After drying under vacuum, 3.8 g (84 %) of a white powder was obtained. TLC (EtOAc/hexane = 1/9): R_f = 0.11; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.88 (t, 6H, C*H*$_3$, *J* = 6.71 Hz), 1.30 (overlapped m, 16H, $CH_3(CH_2)_4$), 1.45 (m, 4H, $CH_2(CH_2)_2O$), 1.76 (m, 4H, CH_2CH_2O), 3.16 (br s, 2H, N*H*$_2$), 4.01 (m, 4H, C*H*$_2$O), 6.15 (d, 1H, Ar*H*, *J* = 1.21 Hz), 6.34 (dd, 1H, Ar*H*, *J* = 8.20 Hz), 6.78 (d, 1H, Ar*H*, meta to NH_2, *J* = 8.20 Hz); ^{13}C

NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.13, 22.74, 26.17-30.12, 31.96, 69.23, 101.78, 107.51, 112.87, 140.42, 142.16, 143.53.

1-Nitro-4-(octyloxy)benzene (49):

Yield 2.5 g (92 %) as yellow oil. TLC (EtOAc/hexane = 1/9): R_f = 0.77; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.88 (t, 3H, C*H*$_3$, *J* = 5.80 Hz), 1.30 (overlapped m, 8H, $CH_3(CH_2)_4$), 1.46 (m, 2H, C*H*$_2$$(CH_2)_2O$), 1.78 (m, 2H, C*H*$_2$$CH_2O$), 4.04 (t, 2H, C*H*$_2$O, *J* = 7.30 Hz), 6.94 (d, 2H, Ar*H*, *meta* to NO_2, *J* = 10.10 Hz), 8.19 (d, 2H, Ar*H*, *ortho* to NO_2, *J* = 9.20 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.07, 22.56, 25.89, 29.26, 29.57, 31.85, 68.68, 115.27, 125.45, 139.49, 165.46.

4-(Octyloxy)aniline (50):

Yield 1.95 g (92 %) as viscous brown oil. TLC (EtOAc/hexane = 1/9): R_f = 0.12; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.89 (t, 3H, C*H*$_3$, *J* = 6.87 Hz), 1.31 (overlapped m, 8H, $CH_3(CH_2)_4$), 1.44 (m, 2H, C*H*$_2$$(CH_2)_2O$), 1.74 (m, 2H, C*H*$_2$$CH_2O$), 3.34 (br s, 2H, N*H*$_2$), 3.88 (t, 2H, C*H*$_2$O, *J* = 6.56 Hz), 6.63 (d, 2H, Ar*H*, *ortho* to NH_2, *J* = 9.50 Hz), 6.74 (d, 2H, Ar*H*, *meta* to NH_2, *J* = 9.20 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.08, 22.68, 25.88, 29.27, 29.58, 31.87, 68.66, 115.18, 115.35, 139.96, 149.38.

1,2,3-Trimethoxy-5-nitrobenzene (51):

To a stirred suspension of $SiO_2 \cdot HNO_3$ (28.1 g, 0.09 mole, 20 % HNO3 w/w) in CH_2Cl_2 (100 mL) at room temperature, 1,2,3-trimethoxybenzene (10 g, 0.06 mole dissolved in 25 mL CH_2Cl_2) was added rapidly. The resulting red solution was stirred for 15 min, filtered

and washed several times with CH_2Cl_2. The solution was concentrated in a rotary evaporator and precipitated in cold MeOH (200 mL). The yellow precipitate was collected by filtration and air-dried. Recrystallization from MeOH-CH_2Cl_2 yielded 3.1 g (25 %) as yellowish-white crystals. TLC (EtOAc/hexane = 3/7): R_f = 0.52; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 3.95 (s, 9H, C*H*$_3$), 7.53 (s, 2H, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 56.68, 61.29, 101.57, 144.09, 153.08.

5-Nitrobenzene-1,2,3-triol (52):

Compound **51** (3.75 g, 0.018 mole) was mixed with pyridine hydrochloride (12.20 g, 0.11 mole) and stirred at 200 °C for 1 hour. The reaction mixture was cooled to below 100 °C and added to water. The solution was extracted with EtOAc three times. The combined extract was washed with dilute HCl, H_2O and finally with brine. The organic phase was dried over anhydrous $MgSO_4$ and evaporated to yield 2.1 g (70 %) as yellow solid. The product was used for the next step without further purification. TLC (EtOAc/hexane = 3/7): R_f = 0.17; ^{1}H NMR (500 MHz, DMSO-d6, 25 °C, TMS): δ = 7.22 (s, 2H, Ar*H*), 9.7 (br s, 3H, O*H*); ^{13}C NMR (125 MHz, DMSO-d6, 25 °C, TMS): δ = 103.01, 138.48, 141.09, 145.38.

3,4,5-Tris(3,4,5-tris(octyloxy)benzyloxy)-1-nitrobenzene (53):

To a thoroughly degassed suspension of anhydrous K_2CO_3 (1.24 g, 0.009 mole) in DMF (25 mL) was added compound **52** (0.26 g, 0.0015 mole) and the reaction mixture was heated to 70 °C which was added compound **28** (2.3 g, 0.0045 mole) under N_2 atmosphere. After stirring for 8 hours at 70 °C, the reaction mixture was poured into ice-cooled water and the precipitate was collected by filtration and vacuum dried. The crude

product was passed through a short column of basic Al_2O_3 using CH_2Cl_2 as eluent. Purification by column chromatography (EtOAc/hexane = 1/9) yielded 2.1 g (88 %). TLC (EtOAc/hexane = 1/9): R_f = 0.60; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.89 (t, 27H, C*H*$_3$, *J* = 7.30 Hz), 1.30 (overlapped m, 72H, $CH_3(CH_2)_4$), 1.44 (m, 18H, $CH_2(CH_2)_2O$), 1.74 (m, 18H, CH_2CH_2O), 3.78 (t, 4H, CH_2O, 4-(3',5') positions, *J* = 6.30 Hz), 3.92 (overlapped t, 14H, CH_2O, 3,5-(3',5') positions, 3,4,5-(4') positions), 5.07 (d, 6H, PhCH_2, *J* = 6.70 Hz), 6.60 (s, 2H, Ar*H*, *ortho* to $PhOCH_2$, 4' position), 6.63 (s, 4H, Ar*H*, *ortho* to $PhOCH_2$, 3',5' positions), 7.59 (s, 2H, Ar*H*, *ortho* to NO_2); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.03, 22.63, 26.08, 29.26, 29.30, 29.36, 29.53, 30.33, 31.80, 31.83, 31.87, 68.93, 69.13, 71.84, 73.33, 73.40, 75.38, 103.68, 105.83, 106.37, 130.80, 131.87, 138.08, 138.18, 143.39, 143.89, 152.48, 153.14, 153.46.

3,4,5-Tris(3,4,5-tris(dodecyloxy)benzyloxy)-1-nitrobenzene (54):

To a thoroughly degassed suspension of anhydrous K_2CO_3 (0.81 g, 0.0059 mole) in DMF (25 mL) was added compound **52** (0.17 g, 0.001 mole) and the reaction mixture was heated to 70 °C which was added compound **29** (2.0 g, 0.003 mole) under N_2 atmosphere. After stirring for 8 hours at 70 °C, the reaction mixture was poured into ice-cooled water and the precipitate was collected by filtration and vacuum dried. The crude product was passed through a short column of basic Al_2O_3 using CH_2Cl_2 as eluent. Purification by column chromatography (EtOAc/hexane = 1/9) yielded 1.8 g (88 %). TLC (EtOAc/hexane = 1/9): R_f = 0.71; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.88 (t, 27H, C*H*$_3$, *J* = 6.41 Hz), 1.26 (overlapped m, 144H, $CH_3(CH_2)_8$), 1.43 (m, 18H, $CH_2(CH_2)_2O$), 1.73 (m, 18H, CH_2CH_2O), 3.77 (t, 4H, CH_2O, 4-(3',5') positions, *J* = 6.45 Hz), 3.91 (overlapped t, 14H, CH_2O, 3,5-(3',5') positions, 3,4,5-(4') positions), 5.06 (s,

4H, PhC*H*$_2$ *meta* to NO_2), 5.08 (s, 2H, PhC*H*$_2$ *para* to NO_2), 6.59 (s, 2H, Ar*H*, *ortho* to $PhOCH_2$, 4' position), 6.63 (s, 4H, Ar*H*, *ortho* to $PhOCH_2$, 3',5' positions), 7.59 (s, 2H, Ar*H*, *ortho* to NO_2); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.05, 22.64, 26.12, 29.36, 29.40, 29.46, 29.53, 29.65, 29.70, 30.36, 31.90, 68.83, 69.04, 71.57, 73.37, 75.54, 96.08, 105.41, 106.32, 131.33, 132.46, 133.20, 137.62, 137.69, 142.83, 153.01, 153.30, 153.59.

3,4,5-Tris(3,4,5-tris(octyloxy)benzyloxy)aniline (55):

A mixture of compound **53** (1.2 g, 0.00075 mole), $NH_2NH_2{\cdot}H_2O$ (0.20 g, 0.0038 mole) and graphite (1.0 g) in EtOH-THF mixture (25 mL, 4:1) was refluxed under N_2 atmosphere for 24 hours. The cooled mixture was diluted with CH_2Cl_2 (20 mL). Graphite was filtered and washed several times with CH_2Cl_2. The colorless solution was concentrated on a rotary evaporator and the resulting white solid was dissolved in CH_2Cl_2. After precipitation in MeOH, the obtained solid was collected by filtration and washed with cold MeOH. After drying under vacuum, 0.9 g (77 %) of a white powder was obtained. TLC (EtOAc/hexane = 3/7): R_f = 0.70; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.89 (t, 27H, C*H*$_3$, *J* = 6.40 Hz), 1.30 (overlapped m, 72H, $CH_3(CH_2)_4$), 1.45 (m, 18H, C*H*$_2(CH_2)_2O$), 1.74 (m, 18H, C*H*$_2CH_2O$), 3.49 (br s, 2H, N*H*$_2$), 3.80 (t, 4H, C*H*$_2$O, 4-(3',5') positions, *J* = 6.41 Hz), 3.90 (overlapped t, 14H, C*H*$_2$O, 3,5-(3',5') positions, 3,4,5-(4') positions), 4.90 (s, 2H, PhC*H*$_2$ *para* to NH_2), 4.96 (s, 4H, PhC*H*$_2$ *meta* to NH_2), 5.99 (s, 2H, Ar*H*, *ortho* to NH_2), 6.61 (s, 4H, Ar*H*, *ortho* to $PhOCH_2$, 3', 5' positions), 6.64 (s, 2H, Ar*H*, *ortho* to $ArOCH_2$, 4' position); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.02, 22.62, 26.08, 29.26, 29.29, 29.37, 29.42, 29.53, 30.33, 31.79,

31.86, 68.81, 69.03, 71.56, 73.28, 73.36, 75.53, 96.05, 105.43, 106.33, 131.31, 132.45, 133.20, 137.62, 137.69, 142.83, 153.00, 153.29, 153.57.

3,4,5-Tris(3,4,5-tris(dodecyloxy)benzyloxy)aniline (56):

A mixture of compound **54** (1.5 g, 0.0007 mole), $NH_2NH_2 \cdot H_2O$ (0.18 g, 0.0036 mole) and graphite (1.0 g) in EtOH-THF mixture (25 mL, 4:1) was refluxed under N_2 atmosphere for 24 hours. The cooled mixture was diluted with CH_2Cl_2 (20 mL). Graphite was filtered and washed several times with CH_2Cl_2. The colorless solution was concentrated on a rotary evaporator and the resulting white solid was dissolved in CH_2Cl_2. After precipitation in MeOH, the obtained solid was collected by filtration and washed with cold MeOH. After drying under vacuum, 1.2 g (80 %) of a white powder was obtained. TLC (EtOAc/hexane = 3/7): R_f = 0.77; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.88 (t, 27H, C*H*$_3$, *J* = 6.87 Hz), 1.27 (overlapped m, 144H, $CH_3(CH_2)_8$), 1.43 (m, 18H, C*H*$_2$$(CH_2)_2O$), 1.73 (m, 18H, C*H*$_2$$CH_2O$), 3.78 (t, 4H, C*H*$_2$O, 4-(3',5') positions, *J* = 7.30 Hz), 3.88 (t, 10H, C*H*$_2$O, 3,5-(3',5') positions, 4-(4') position, *J* = 6.40 Hz), 3.92 (t, 4H, C*H*$_2$O, 3,5-(4') positions, *J* = 6.60 Hz), 4.89 (s, 2H, PhC*H*$_2$ *para* to NH_2), 4.95 (s, 4H, PhC*H*$_2$ *meta* to NH_2), 5.99 (s, 2H, Ar*H*, *ortho* to NH_2), 6.60 (s, 4H, Ar*H*, *ortho* to $PhOCH_2$, 3', 5' positions), 6.63 (s, 2H, Ar*H*, *ortho* to $PhOCH_2$, 4' position); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.05, 22.64, 26.12, 29.36, 29.40, 29.46, 29.53, 29.65, 29.70, 30.36, 31.90, 68.83, 69.04, 71.57, 73.37, 75.54, 96.08, 105.41, 106.32, 131.33, 132.46, 133.20, 137.62, 137.69, 142.83, 153.01, 153.30, 153.59.

3,4,5-Tris(octyloxy)-N-(3,4,5-tris(octyloxy)phenyl)benzamide (57):

In a 50 mL two neck flask, compound **11** (1.27 g, 0.0025 mole) was dissolved in dry THF (20 mL). After adding CDMT (0.48 g, 0.0028 mole) and NMM (0.38 g, 0.0038 mole), the mixture was stirred for 1 hour at room temperature under N_2 atmosphere. Then compound **44** (1.20 g, 0.0025 mole) was added and the reaction mixture was further stirred for 6 hours at room temperature. The mixture was diluted with CH_2Cl_2 (10 mL) and precipitated in methanol (100 mL) and the product was collected by filtration and dried. Purification by column chromatography (EtOAc/Hexane = 1/9) followed by precipitation in methanol yielded 1.32 g (54 %). TLC (EtOAc/hexane = 1/9): R_f = 0.40; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.89 (t, 18H, C*H*$_3$, *J* = 6.87 Hz), 1.31 (overlapped m, 48H, $CH_3(CH_2)_4$), 1.48 (m, 12H, C*H*$_2$$(CH_2)_2O$), 1.79 (m, 12H, C*H*$_2$$CH_2O$), 3.94 (t, 2H, C*H*$_2$O *para* to NH, *J* = 5.80 Hz), 4.01 (overlapped t, 10H, C*H*$_2$O), 6.91 (s, 2H, Ar*H*, *ortho* to NH), 7.03 (s, 2H, Ar*H*, *ortho* to CO), 7.64 (s, 1H, N*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.02, 22.60, 26.01, 29.22, 29.31, 29.46, 29.51, 30.25, 31.77, 31.84, 69.14, 69.47, 73.51, 73.54, 99.15, 105.77, 129.95, 133.57, 135.06, 141.58, 153.30, 165.55.

3,4,5-Tris(11-hydroxyundecyloxy)-N-(3,4,5-tris(octyloxy)phenyl)benzamide (58):

In a 50 mL two neck flask, compound **13** (1.36 g, 0.002 mole) was dissolved in dry THF (20 mL). After adding CDMT (0.39 g, 0.0022 mole) and NMM (0.31 g, 0.003 mole), the mixture was stirred for 1 hour at room temperature under N_2 atmosphere. Then compound **44** (0.96 g, 0.002 mole) was added and the reaction mixture was further stirred for 6 hours at room temperature. The mixture was diluted with CH_2Cl_2 (10 mL) and

precipitated in methanol (100 mL) and the product was collected by filtration and dried. Purification by column chromatography (EtOAc/Hexane = 7/3) followed by precipitation in methanol yielded 1.4 g (61 %). TLC (EtOAc/hexane = 7/3): R_f = 0.56; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.88 (t, 9H, C*H*$_3$, *J* = 6.40 Hz), 1.30 (overlapped m, 60H, $CH_3(CH_2)_4$, $(CH_2)_6CH_2CH_2OH$), 1.47 (m, 15H, C*H*$_2$$(CH_2)_2O$, O*H*), 1.56 (m, 6H, C*H*$_2$$CH_2OH$), 1.79 (overlapped m, 12H, C*H*$_2$$CH_2O$), 3.64 (t, 6H, C*H*$_2$OH, *J* = 6.60 Hz), 3.93 (t, 2H, C*H*$_2$O *para* to NH, *J* = 6.10 Hz), 4.01 (overlapped t, 10H, C*H*$_2$O), 6.91 (s, 2H, Ar*H*, *ortho* to NH), 7.04 (s, 2H, Ar*H*, *ortho* to CO), 7.68 (s, 1H, N*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.02, 22.60, 25.68, 25.99, 26.02, 26.06, 29.23, 29.31, 29.36, 29.41, 29.45, 29.51, 29.59, 30.24, 31.78, 31.85, 32.73, 63.00, 69.14, 69.43, 73.51, 99.19, 105.79, 129.98, 133.59, 135.05, 141.52, 153.26, 165.60.

3,4,5-Tris(dodecyloxy)-N-(3,4,5-tris(dodecyloxy)phenyl)benzamide (59):

In a 50 mL two neck flask, compound **AN-12** (1.35 g, 0.002 mole) was dissolved in dry THF (20 mL). After adding CDMT (0.39 g, 0.0022 mole) and NMM (0.31 g, 0.003 mole), the mixture was stirred for 1 hour at room temperature under N_2 atmosphere. Then compound **45** (1.30 g, 0.002 mole) was added and the reaction mixture was further stirred for 6 hours at room temperature. The mixture was diluted with CH_2Cl_2 (10 mL) and precipitated in methanol (100 mL) and the product was collected by filtration and dried. Purification by column chromatography (EtOAc/Hexane = 1/9) followed by precipitation in methanol yielded 2.4 g (92 %). TLC (EtOAc/hexane = 1/9): R_f = 0.79; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.89 (t, 18H, C*H*$_3$, *J* = 7.02 Hz), 1.31 (overlapped m, 96H, $CH_3(CH_2)_8$), 1.48 (m, 12H, C*H*$_2$$(CH_2)_2O$), 1.79 (m, 12H, C*H*$_2$$CH_2O$), 3.94 (t, 2H, C*H*$_2$O *para* to NH, *J* = 6.56 Hz), 4.01 (overlapped t, 10H, C*H*$_2$O), 6.90 (s, 2H, Ar*H*,

ortho to NH), 7.03 (s, 2H, Ar*H*, *ortho* to CO), 7.59 (s, 1H, N*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.05, 22.63, 26.03, 29.32, 29.60, 29.65, 30.27, 31.88, 69.46, 69.47, 73.51, 73.55, 99.15, 105.78, 129.96, 133.56, 135.08, 141.60, 153.31, 165.54.

3,4,5-Tris(11-hydroxyundecyloxy)-N-(3,4,5-tris(dodecyloxy)phenyl)benzamide (60):

In a 50 mL two neck flask, compound **13** (1.36 g, 0.002 mole) was dissolved in dry THF (20 mL). After adding CDMT (0.39 g, 0.0022 mole) and NMM (0.31 g, 0.003 mole), the mixture was stirred for 1 hour at room temperature under N_2 atmosphere. Then compound **45** (1.30 g, 0.002 mole) was added and the reaction mixture was further stirred for 6 hours at room temperature. The mixture was diluted with THF (10 mL) and precipitated in methanol (100 mL) and the product was collected by filtration and dried. Purification by column chromatography (EtOAc/Hexane = 7/3) followed by precipitation in methanol yielded 2.2 g (85 %). TLC (EtOAc/hexane = 7/3): R_f = 0.75; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.88 (t, 9H, C*H*$_3$, *J* = 6.87 Hz), 1.29 (overlapped m, 84H, $CH_3(CH_2)_8$, $(CH_2)_6CH_2CH_2OH$), 1.47 (m, 12H, C*H*$_2$$(CH_2)_2O$), 1.56 (m, 6H, C*H*$_2$$CH_2OH$), 1.78 (overlapped m, 12H, C*H*$_2$$CH_2O$), 3.49 (s, 3H, O*H*), 3.63 (t, 6H, C*H*$_2$OH, *J* = 6.56 Hz), 3.93 (t, 2H, C*H*$_2$O *para* to NH, *J* = 6.56 Hz), 4.00 (overlapped t, 10H, C*H*$_2$O), 6.90 (s, 2H, Ar*H*, *ortho* to NH), 7.04 (s, 2H, Ar*H*, *ortho* to CO), 7.71 (s, 1H, N*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.03, 22.62, 25.68, 25.99, 26.04, 26.08, 29.30, 29.36, 29.45, 29.51, 29.59, 29.64, 29.69, 30.24, 31.87, 32.72, 62.99, 69.14, 69.42, 73.51, 99.19, 105.79, 129.98, 133.59, 135.04, 141.51, 153.25, 165.60.

3,4,5-Tris(2-(2-methoxyethoxy)ethoxy)-N-(3,4,5-tris(dodecyloxy)phenyl)benzamide (61):

In a 100 mL two neck flask, compound **20** (1.43 g, 0.003 mole) was dissolved in dry THF (40 mL). After adding CDMT (0.58 g, 0.0033 mole) and NMM (0.46 g, 0.0045 mole), the mixture was stirred for 1 hour at room temperature under N_2 atmosphere. Then compound **45** (1.49 g, 0.003 mole) was added and the reaction mixture was further stirred for 6 hours at room temperature. The mixture was diluted with CH_2Cl_2 (15 mL) and precipitated in methanol (100 mL) and the product was collected by filtration and dried. Purification by column chromatography (EtOAc/Hexane = 2/8) followed by precipitation in methanol yielded 1.98 g (60 %). TLC (EtOAc/hexane = 2/8): R_f = 0.41; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.88 (t, 9H, C*H*$_3$, *J* = 6.71 Hz), 1.28 (overlapped m, 48H, $CH_3(CH_2)_8$), 1.46 (m, 6H, C*H*$_2$$(CH_2)_2O$), 1.78 (m, 6H, C*H*$_2$$CH_2O$), 3.36 (s, 6H, OC*H*$_3$ *meta* to CO), 3.39 (s, 3H, OC*H*$_3$ *para* to CO), 3.57 (m, 6H, CH_3OCH_2), 3.72 (m, 6H, $CH_3OCH_2CH_2$), 3.82 (t, 2H, OCH_2CH_2 *para* to CO, *J* = 5.04 Hz), 3.86 (t, 4H, OCH_2CH_2 *meta* to CO, *J* = 4.88 Hz), 3.93 (t, 2H, OC*H*$_2$ *para* to NH, *J* = 6.56 Hz), 3.99 (t, 4H, OC*H*$_2$ *meta* to NH, *J* = 6.56 Hz), 4.25 (overlapped t, 6H, OC*H*$_2$ *meta* and *para* to CO), 6.96 (s, 2H, Ar*H*, *ortho* to NH), 7.19 (s, 2H, Ar*H*, *ortho* to CO), 7.98 (s, 1H, N*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.04, 22.62, 26.03, 26.07, 29.30, 29.36, 29.59, 29.64, 29.69, 30.24, 31.86, 58.87, 58.99, 69.04, 69.20, 69.77, 70.41, 70.48, 70.52, 71.85, 71.99, 72.44, 73.48, 99.07, 107.56, 130.13, 133.79, 134.84, 141.87, 152.61, 153.19, 165.17.

3,4,5-Tris(2-(2-butoxyethoxy)ethoxy)-N-(3,4,5-tris(dodecyloxy)phenyl)benzamide (62):

In a 100 mL two neck flask, compound **23** (0.90 g, 0.0015 mole) was dissolved in dry THF (30 mL). After adding CDMT (0.29 g, 0.0016 mole) and NMM (0.23 g, 0.0023 mole), the mixture was stirred for 1 hour at room temperature under N_2 atmosphere. Then compound **45** (0.97 g, 0.0015 mole) was added and the reaction mixture was further stirred for 6 hours at room temperature. The mixture was diluted with CH_2Cl_2 (15 mL) and precipitated in methanol (80 mL) and the product was collected by filtration and dried. Purification by column chromatography (EtOAc/Hexane = 3/7) followed by precipitation in methanol yielded 1.11 g (60 %). TLC (EtOAc/hexane = 3/7): R_f = 0.44; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.89 (overlapped t, 18H, C*H*$_3$), 1.31 (overlapped m, 54H, $CH_3(CH_2)_8$, CH_3CH_2), 1.46 (m, 6H, C*H*$_2$(CH$_2$)$_2$O), 1.54 (m, 2H, $CH_3CH_2CH_2$), 1.78 (m, 6H, C*H*$_2$CH$_2$O), 3.46 (m, 2H, $CH_3CH_2CH_2CH_2$), 3.60 (m, 6H, $CH_3CH_2CH_2CH_2OCH_2$), 3.71 (t, 6H, $CH_3CH_2CH_2CH_2OCH_2CH_2$, *J* = 5.20 Hz), 3.82 (t, 2H, OCH$_2$C*H*$_2$ *para* to CO, *J* = 5.20 Hz), 3.87 (t, 4H, OCH$_2$C*H*$_2$ *meta* to CO, *J* = 4.60 Hz), 3.93 (t, 2H, OC*H*$_2$ *para* to NH, *J* = 6.60 Hz), 3.99 (t, 4H, OC*H*$_2$ *meta* to NH, *J* = 6.40 Hz), 4.24 (overlapped t, 6H, OC*H*$_2$ *meta* and *para* to CO), 6.95 (s, 2H, Ar*H*, *ortho* to NH), 7.19 (s, 2H, Ar*H*, *ortho* to CO), 7.92 (s, 1H, N*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 13.83, 13.86, 14.05, 19.17, 19.21, 22.63, 26.05, 26.09, 29.32, 29.37, 29.60, 29.65, 29.70, 30.26, 31.57, 31.68, 31.88, 69.09, 69.32, 69.82, 70.01, 70.14, 70.52, 70.56, 70.64, 71.13, 71.24, 72.46, 73.51, 99.08, 107.57, 130.18, 133.78, 134.92, 141.95, 152.72, 153.21, 153.24, 165.22.

N-(3,4-bis(octyloxy)phenyl)-3,4-bis(octyloxy)benzamide (63):

In a 50 mL two neck flask, compound **16** (1.51 g, 0.004 mole) was dissolved in dry THF (25 mL). After adding CDMT (0.77 g, 0.0044 mole) and NMM (0.61 g, 0.006 mole), the mixture was stirred for 1 hour at room temperature under N_2 atmosphere. Then compound **48** (1.40 g, 0.004 mole) was added and the reaction mixture was further stirred for 6 hours at room temperature. The mixture was diluted with CH_2Cl_2 (10 mL) and precipitated in methanol (100 mL) and the product was collected by filtration and dried. Purification by column chromatography (EtOAc/Hexane = 2/8) followed by precipitation in methanol yielded 1.65 g (58 %). TLC (EtOAc/hexane = 2/8): R_f = 0.45; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.88 (t, 12H, C*H*$_3$, *J* = 6.87 Hz), 1.31 (overlapped m, 32H, $CH_3(CH_2)_4$), 1.47 (m, 8H, C*H*$_2$$(CH_2)_2O$), 1.78 (m, 8H, C*H*$_2$$CH_2O$), 4.01 (m, 8H, C*H*$_2$O), 6.14 (d, 1H, Ar*H*, *J* = 1.21 Hz), 6.25 (dd, 1H, Ar*H*, *J* = 8.20 Hz), 6.71 (d, 1H, Ar*H*, meta to NH, *J* = 8.20 Hz), 7.11 (d, 1H, Ar*H*, meta to CO, *J* = 8.20 Hz), 7.39 (d, 1H, Ar*H*, *J* = 1.28 Hz), 7.54 (dd, 1H, Ar*H*, *J* = 8.20 Hz), 7.85 (s, 1H, N*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.07, 22.61, 26.04, 29.26, 29.37, 29.49, 29.56, 30.27, 31.78, 31.85, 69.15, 69.48, 105.46, 111.61, 111.94, 113.82, 114.05,119.81, 126.45, 130.51, 143.46, 146.38, 149.43, 154.13, 164.65.

N-(3,4-bis(octyloxy)phenyl)-3,4-bis(11-hydroxyundecyloxy)benzamide (64):

In a 50 mL two neck flask, compound **17** (1.98 g, 0.004 mole) was dissolved in dry THF (25 mL). After adding CDMT (0.77 g, 0.0044 mole) and NMM (0.61 g, 0.006 mole), the mixture was stirred for 1 hour at room temperature under N_2 atmosphere. Then compound **48** (1.40 g, 0.004 mole) was added and the reaction mixture was further stirred

for 6 hours at room temperature. The mixture was diluted with CH_2Cl_2 (10 mL) and precipitated in methanol (100 mL) and the product was collected by filtration and dried. Purification by column chromatography (EtOAc/Hexane = 7/3) followed by precipitation in methanol yielded 1.7 g (51 %). TLC (EtOAc/hexane = 7/3): R_f = 0.50; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.88 (t, 6H, C*H*$_3$, *J* = 6.45 Hz), 1.31 (overlapped m, 40H, $CH_3(CH_2)_4$, $(CH_2)_6CH_2CH_2OH$), 1.47 (m, 11H, C*H*$_2$$(CH_2)_2O$, O*H*), 1.56 (m, 4H, C*H*$_2$$CH_2OH$), 1.79 (overlapped m, 8H, C*H*$_2$$CH_2O$), 3.65 (t, 4H, C*H*$_2$OH, *J* = 6.65 Hz), 4.01 (m, 8H, C*H*$_2$O), 6.15 (d, 1H, Ar*H*, *J* = 1.25 Hz), 6.24 (dd, 1H, Ar*H*, *J* = 8.25 Hz), 6.72 (d, 1H, Ar*H*, meta to NH, *J* = 8.25 Hz), 7.13 (d, 1H, Ar*H*, meta to CO, *J* = 8.25 Hz), 7.38 (d, 1H, Ar*H*, *J* = 1.25 Hz), 7.53 (dd, 1H, Ar*H*, *J* = 8.25 Hz), 7.84 (s, 1H, N*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.01, 22.61, 25.67, 25.98, 26.01, 26.05, 29.22, 29.30, 29.35, 29.41, 29.45, 29.51, 29.59, 30.25, 31.78, 31.85, 32.73, 63.00, 69.15, 69.45, 105.45, 111.62, 111.95, 113.83, 114.07,119.84, 126.48, 130.53, 143.47, 146.35, 149.44, 154.17, 164.63.

3,4,5-Tris(dodecyloxy)-N-(4-(octyloxy)phenyl)benzamide (65):

In a 50 mL two neck flask, compound **12** (1.20 g, 0.0018 mole) was dissolved in dry THF (20 mL). After adding CDMT (0.35 g, 0.002 mole) and NMM (0.27 g, 0.0027 mole), the mixture was stirred for 1 hour at room temperature under N_2 atmosphere. Then compound **50** (0.39 g, 0.0018 mole) was added and the reaction mixture was further stirred for 6 hours at room temperature. The mixture was diluted with CH_2Cl_2 (10 mL) and precipitated in methanol (75 mL) and the product was collected by filtration and dried. Purification by column chromatography (EtOAc/Hexane = 1/9) followed by precipitation in methanol yielded 0.93 g (60 %). TLC (EtOAc/hexane = 1/9): R_f = 0.38;

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.89 (t, 12H, C*H*$_3$, *J* = 6.26 Hz), 1.29 (overlapped m, 56H, $CH_3(CH_2)_4$, $CH_3(CH_2)_8$), 1.46 (m, 8H, $CH_2(CH_2)_2O$), 1.79 (m, 8H, CH_2CH_2O), 3.95 (t, 2H, CH_2O, *para* to NH, *J* = 6.70 Hz), 4.02 (overlapped t, 6H, CH_2O, *meta* and *para* to CO), 6.90 (d, 2H, Ar*H*, *meta* to NH, *J* = 8.85 Hz), 7.04 (s, 2H, Ar*H*, *ortho* to CO), 7.51 (d, 2H, Ar*H*, *ortho* to NH, *J* = 8.85 Hz), 7.66 (s, 1H, N*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.05, 22.64, 26.03, 29.19, 29.24, 29.32, 29.60, 29.65, 29.69, 30.27, 31.77, 31.88, 68.32, 69.45, 73.54, 105.82, 114.90, 122.02, 130.08, 130.91, 141.45, 153.29, 156.23, 165.60.

3,4,5-tris(octyloxy)benzyl 3,4,5-tris(octyloxy)benzoate (66):

In a 50 mL two neck flask, compound **11** (1.01 g, 0.0021 mole) and compound **24** (1.23 g, 0.0025 mole) were dissolved in dry CH_2Cl_2 (15 mL). After adding DCC (0.52 g, 0.0025 mole) and DPTS (0.12 g, 0.0004 mole), the mixture was stirred for 3 hours at room temperature under N_2 atmosphere. The mixture was diluted with CH_2Cl_2 (10 mL) and precipitated in methanol (100 mL) and the product was collected by filtration and dried. Purification by column chromatography (EtOAc/Hexane = 1/9) followed by precipitation in methanol yielded 1.32 g (54 %). TLC (EtOAc/hexane = 1/9): R_f = 0.51; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.88 (t, 18H, C*H*$_3$, *J* = 5.80 Hz), 1.30 (overlapped m, 48H, $CH_3(CH_2)_4$), 1.47 (m, 12H, $CH_2(CH_2)_2O$), 1.79 (m, 12H, CH_2CH_2O), 3.99 (overlapped t, 12H, CH_2O), 5.24 (s, 2H, $PhCO_2CH_2$), 6.63 (s, 2H, Ar*H*, *ortho* to $PhCO_2CH_2$), 7.29 (s, 2H, Ar*H*, *ortho* to CO_2); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.02, 22.60, 25.98, 26.05, 29.23, 29.27, 29.30, 29.32, 29.44, 29.49, 30.27, 31.77, 31.83, 66.93, 69.12, 69.18, 73.42, 73.49, 106.82, 108.16, 124.71, 131.19, 138.18, 142.56, 152.89, 153.25, 166.39.

3,4,5-tris(octyloxy)benzyl 3,4,5-tris(11-hydroxyundecyloxy)benzoate (67):

In a 50 mL two neck flask, compound **13** (1.36 g, 0.002 mole) and compound **24** (1.0 g, 0.002 mole) were dissolved in dry CH_2Cl_2 (15 mL). After adding DCC (0.50 g, 0.0024 mole) and DPTS (0.12 g, 0.0004 mole), the mixture was stirred for 1.5 hours at room temperature under N_2 atmosphere. The mixture was diluted with CH_2Cl_2 (10 mL) and precipitated in hexane (100 mL) and the product was collected by filtration and dried. Purification by column chromatography (EtOAc/Hexane = 7/3) followed by precipitation in hexane yielded 1.5 g (65 %). TLC (EtOAc/hexane = 7/3): R_f = 0.70; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.88 (t, 9H, C*H*$_3$, *J* = 6.40 Hz), 1.19 (overlapped m, 60H, $CH_3(CH_2)_4$, $(CH_2)_6CH_2CH_2OH$), 1.47 (m, 12H, $CH_2(CH_2)_2O$), 1.56 (m, 6H, CH_2CH_2OH), 1.74 (overlapped m, 12H, CH_2CH_2O), 3.63 (t, 6H, CH_2OH, *J* = 6.10 Hz), 3.99 (tt, 12H, CH_2O, *J* = 12.44, 6.03 Hz), 5.23 (s, 2H, $PhCO_2CH_2$), 6.62 (s, 2H, Ar*H*, *ortho* to $PhCO_2CH_2$), 7.28 (s, 2H, Ar*H*, *ortho* to CO_2); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.00, 22.58, 25.68, 26.02, 29.22, 29.29, 29.36, 29.46, 29.52, 30.23, 31.74, 32.71, 62.94, 69.09, 73.41, 73.44, 106.77, 108.10, 124.69, 131.15, 138.11, 142.48, 152.85, 153.21, 166.39.

3,4,5-Tris(3,4,5-tris(octyloxy)benzyloxy)-N-(3,4,5-tris(octyloxy)phenyl)benzamide (68):

In a 50 mL two neck flask, compound **36** (1.00 g, 0.00063 mole) was dissolved in dry THF (20 mL). After adding CDMT (0.121 g, 0.00069 mole) and NMM (0.092 g, 0.00095 mole), the mixture was stirred for 1 hour at room temperature under N_2 atmosphere. Then compound **44** (0.30 g, 0.00063 mole) was added and the reaction mixture was further

stirred for 6 hours at room temperature. The mixture was diluted with CH_2Cl_2 (5 mL) and precipitated in methanol (75 mL) and the product was collected by filtration and dried. Purification by column chromatography (EtOAc/Hexane = 1/9) followed by precipitation in methanol yielded 0.65 g (50 %). TLC (EtOAc/hexane = 1/9): R_f = 0.55; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.88 (t, 36H, C*H*$_3$, *J* = 6.40 Hz), 1.28 (overlapped m, 96H, $CH_3(CH_2)_4$), 1.44 (m, 24H, C*H*$_2$$(CH_2)_2O$), 1.73 (m, 24H, C*H*$_2$$CH_2O$), 3.77 (t, 4H, C*H*$_2$O, CO side, 4-(3',5') positions, *J* = 6.30 Hz), 3.88 (overlapped t, 10H, OC*H*$_2$, CO side, 3,5-(3',5') positions, 4-(4') position), 3.94 (t, 6H, C*H*$_2$O, NH side, *J* = 6.40 Hz), 3.98 (t, 4H, OC*H*$_2$, CO side, 3,5-(4') positions, *J* = 6.30 Hz), 5.06 (s, 6H, PhC*H*$_2$), 6.63 (s, 2H, Ar*H*, *ortho* to $PhOCH_2$, 4' position), 6.65 (s, 4H, Ar*H*, *ortho* to $PhOCH_2$, 3',5' positions), 6.86 (s, 2H, Ar*H*, *ortho* to NH), 7.14 (s, 2H, Ar*H*, *ortho* to CO), 7.45 (s, 1H, N*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.33, 22.43, 26.22, 29.37, 29.05, 29.53, 29.78, 30.28, 32.40, 68.90, 69.11, 72.05, 73.32, 73.40, 73.51, 75.27, 99.02, 105.76, 106.36, 107.58, 130.49, 131.66, 132.33, 133.41, 135.14, 137.93, 138.01, 141.75, 153.00, 153.11, 153.35, 153.41, 165.06.

3,4,5-Tris(3,4,5-tris(dodecyloxy)benzyloxy)-N-(3,4,5-tris(dodecyloxy)phenyl)benzamide (69):

In a 50 mL two neck flask, compound **37** (0.93 g, 0.00044 mole) was dissolved in dry THF (20 mL). After adding CDMT (0.086 g, 0.00049 mole) and NMM (0.067 g, 0.00066 mole), the mixture was stirred for 1 hour at room temperature under N_2 atmosphere. Then compound **45** (0.29 g, 0.00044 mole) was added and the reaction mixture was further stirred for 6 hours at room temperature. The mixture was diluted with CH_2Cl_2 (10 mL) and precipitated in methanol (75 mL) and the product was collected by filtration and

dried. Purification by column chromatography (EtOAc/Hexane = 1/9) followed by precipitation in methanol yielded 0.62 g (52 %). TLC (EtOAc/hexane = 1/9): R_f = 0.61; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.88 (t, 36H, C*H*$_3$, *J* = 6.60 Hz), 1.26 (overlapped m, 192H, $CH_3(CH_2)_8$), 1.44 (m, 24H, C*H*$_2$$(CH_2)_2O$), 1.76 (m, 24H, C*H*$_2$$CH_2O$), 3.78 (t, 4H, C*H*$_2$O, CO side, 4-(3',5') positions, *J* = 6.30 Hz), 3.89 (overlapped t, 10H, OC*H*$_2$, CO side, 3,5-(3',5') positions, 4-(4') position), 3.93 (t, 6H, C*H*$_2$O, NH side, *J* = 6.40 Hz), 3.99 (t, 4H, OC*H*$_2$, CO side, 3,5-(4') positions, *J* = 6.30 Hz), 5.05 (s, 6H, PhC*H*$_2$), 6.62 (s, 2H, Ar*H*, *ortho* to $PhOCH_2$, 4' position), 6.63 (s, 4H, Ar*H*, *ortho* to $PhOCH_2$, 3',5' positions), 6.86 (s, 2H, Ar*H*, *ortho* to NH), 7.13 (s, 2H, Ar*H*, *ortho* to CO), 7.46 (s, 1H, N*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.03, 22.63, 26.12, 29.36, 29.45, 29.53, 29.65, 30.28, 30.36, 31.89, 68.90, 69.11, 72.05, 73.32, 73.40, 73.51, 75.27, 99.02, 105.76, 106.36, 107.58, 130.49, 131.66, 132.33, 133.41, 135.14, 137.93, 138.01, 141.75, 153.00, 153.11, 153.35, 153.41, 165.06.

3,4,5-Tris(3,4,5-tris(2-(2-methoxyethoxy)ethoxy)benzyloxy)-N-(3,4,5-tris(3,4,5-tris(dodecyloxy)benzyloxy)phenyl)benzamide (70):

In a 50 mL two neck flask, compound **38** (0.58 g, 0.00039 mole) was dissolved in dry THF (20 mL). After adding CDMT (0.075 g, 0.00043 mole) and NMM (0.059 g, 0.00058 mole), the mixture was stirred for 1 hour at room temperature under N_2 atmosphere. Then compound **56** (0.80 g, 0.00039 mole) was added and the reaction mixture was further stirred for 6 hours at room temperature. The mixture was diluted with CH_2Cl_2 (10 mL) and precipitated in methanol (75 mL) and the product was collected by filtration and dried. Purification by column chromatography (MeOH/CH_2Cl_2 = 0-1 %) followed by precipitation in methanol yielded 0.82 g (60 %). TLC (MeOH/CH_2Cl_2 = 5 %): R_f = 0.44;

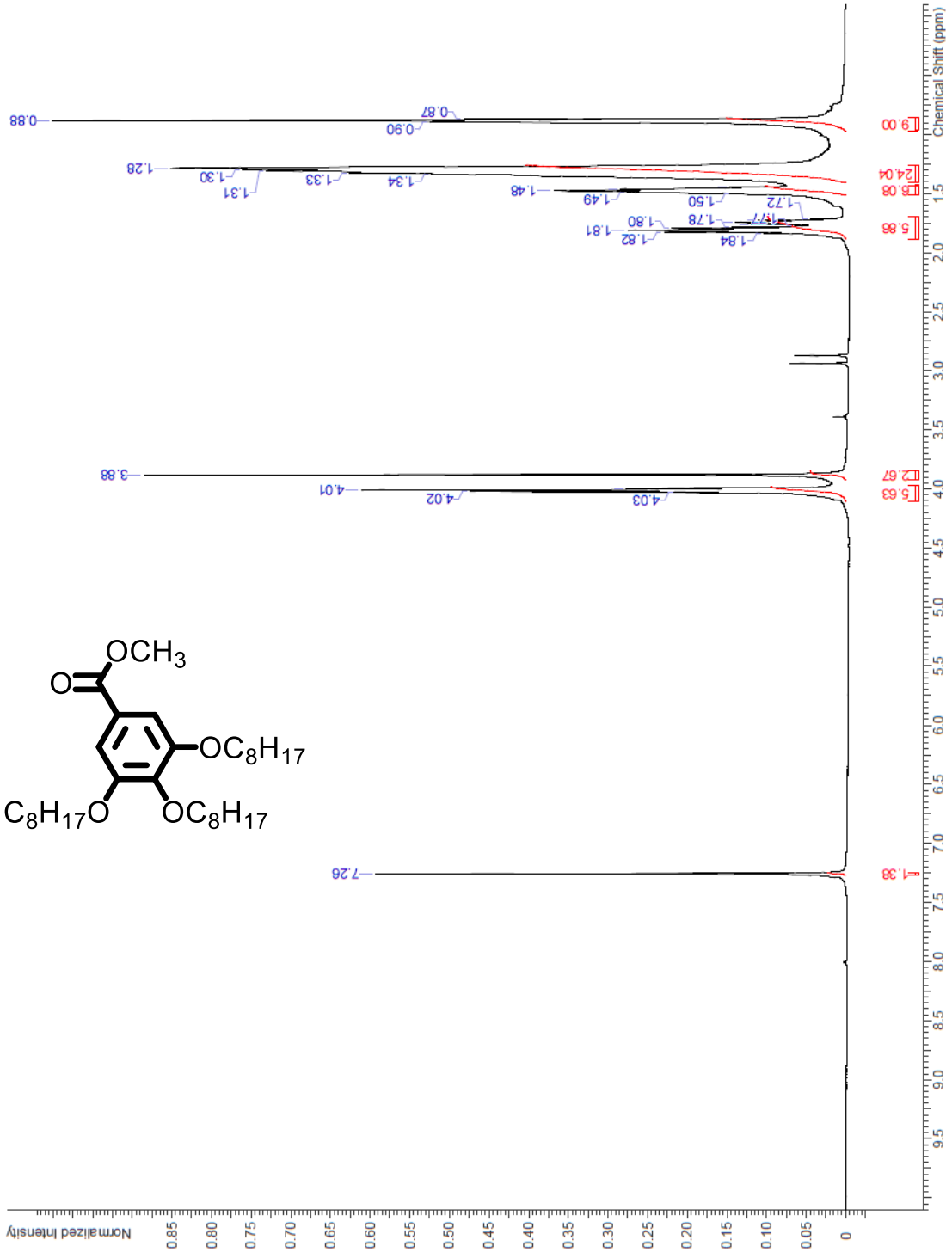
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.89 (t, 27H, C*H*$_3$, *J* = 6.70 Hz), 1.26 (overlapped m, 144H, $CH_3(CH_2)_8$), 1.43 (m, 18H, C*H*$_2(CH_2)_2O$), 1.72 (m, 18H, C*H*$_2CH_2O$), 3.36 (m, 27H, OC*H*$_3$), 3.53 (m, 18H, CH_3OCH_2), 3.70 (m, 18H, $CH_3OCH_2CH_2$), 3.80 (m, 18H, OCH_2CH_2), 3.86 (overlapped t, 14H, C*H*$_2$O, NH Side, 3,5-(3',5') positions, 3,4,5-(4') positions), 3.92 (t, 4H, OC*H*$_2$, NH side, 4-(3',5') positions, *J* = 6.71 Hz), 3.98 (t, 4H, OC*H*$_2$, CO side, 4-(3',5') positions, *J* = 4.58 Hz), 4.12 (overlapped t, 10H, OC*H*$_2$, CO side, 3,5-(3',5') positions, 4-(4') position), 4.16 (t, 4H, OC*H*$_2$, CO side, 3,5-(4') positions, *J* = 5.04 Hz), 4.95 (s, 2H, PhC*H*$_2$, 4' position), 5.04 (br d, 10H, PhC*H*$_2$, 3',5' and 3',4',5' positions, *J* = 9.77 Hz), 6.62 (d, 4H, Ar*H*, *ortho* to $PhOCH_2$, 4' position, *J* = 4.58 Hz), 6.66 (br d, 8H, Ar*H*, *ortho* to $PhOCH_2$, 3',5' positions, *J* = 13.12 Hz), 7.08 (s, 2H, Ar*H*, *ortho* to NH), 7.17 (s, 2H, Ar*H*, *ortho* to CO), 7.97 (s, 1H, N*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.03, 22.63, 26.14, 29.35, 29.43, 29.48, 29.65, 30.37, 31.88, 58.96, 68.67, 68.80, 68.88, 69.01, 69.61, 69.72, 70.37, 70.56, 70.59, 70.64, 71.60, 71.83, 71.94, 72.02, 72.33, 72.39, 73.27, 73.36, 74.89, 100.87, 105.64, 106.00, 106.93, 107.39, 108.05, 132.00, 132.11, 137.65, 137.77, 138.18, 152.48, 152.80, 152.86, 152.99, 153.04, 153.08, 153.24, 153.28, 166.57.

3,4,5-Tris(3,4,5-tris(2-(2-butoxyethoxy)ethoxy)benzyloxy)-N-(3,4,5-tris(3,4,5-tris(dodecyloxy)benzyloxy)phenyl)benzamide (71):

In a 50 mL two neck flask, compound **39** (0.75 g, 0.0004 mole) was dissolved in dry THF (20 mL). After adding CDMT (0.077 g, 0.00044 mole) and NMM (0.061 g, 0.0006 mole), the mixture was stirred for 1 hour at room temperature under N_2 atmosphere. Then compound **56** (0.83 g, 0.0004 mole) was added and the reaction mixture was further stirred for 6 hours at room temperature. The mixture was diluted with CH_2Cl_2 (10 mL)

and precipitated in methanol (75 mL) and the product was collected by filtration and dried. Purification by column chromatography (EtOAc/Hexane = 6/4) followed by precipitation in methanol yielded 0.94 g (60 %). TLC (EtOAc/hexane = 7/3): R_f = 0.51; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.90 (overlapped t, 54H, C*H*$_3$), 1.26 (overlapped m, 144H, $CH_3(CH_2)_8$), 1.35 (m, 18H, CH_3CH_2), 1.43 (m, 18H, $CH_2(CH_2)_2O$), 1.56 (m, 18H, $CH_3CH_2CH_2$), 1.72 (m, 18H, CH_2CH_2O), 3.45 (m, 18H, $CH_3CH_2CH_2CH_2$), 3.58 (m, 18H, $CH_3CH_2CH_2CH_2OCH_2$), 3.70 (m, 18H, $CH_3CH_2CH_2CH_2OCH_2CH_2$), 3.82 (m, 18H, OCH_2CH_2), 3.86 (overlapped t, 14H, CH_2O, NH Side, 3,5-(3',5') positions, 3,4,5-(4') positions), 3.92 (t, 4H, OCH_2, NH side, 4-(3',5') positions, *J* = 6.71 Hz), 3.98 (t, 4H, OCH_2, CO side, 4-(3',5') positions, *J* = 4.58 Hz), 4.12 (overlapped t, 10H, OCH_2, CO side, 3,5-(3',5') positions, 4-(4') position), 4.16 (t, 4H, OCH_2, CO side, 3,5-(4') positions, *J* = 5.04 Hz), 4.95 (s, 2H, $PhCH_2$, 4' position), 5.04 (br d, 10H, $PhCH_2$, 3',5' and 3',4',5' positions, *J* = 9.77 Hz), 6.62 (d, 4H, Ar*H*, *ortho* to $PhOCH_2$, 4' position, *J* = 4.58 Hz), 6.66 (br d, 8H, Ar*H*, *ortho* to $PhOCH_2$, 3',5' positions, *J* = 13.12 Hz), 7.08 (s, 2H, Ar*H*, *ortho* to NH), 7.17 (s, 2H, Ar*H*, *ortho* to CO), 7.97 (s, 1H, N*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 13.74, 14.03, 19.09, 22.63, 26.14, 29.35, 29.43, 29.48, 29.65, 30.37, 31.53, 31.88, 68.67, 68.80, 68.88, 69.01, 69.61, 69.72, 70.37, 70.56, 70.59, 70.64, 71.60, 71.83, 71.94, 72.02, 72.33, 72.39, 73.27, 73.36, 74.89, 100.87, 105.64, 106.00, 106.93, 107.39, 108.05, 132.00, 132.11, 137.65, 137.77, 138.18, 152.48, 152.80, 152.86, 152.99, 153.04, 153.08, 153.24, 153.28, 166.57.

Appendix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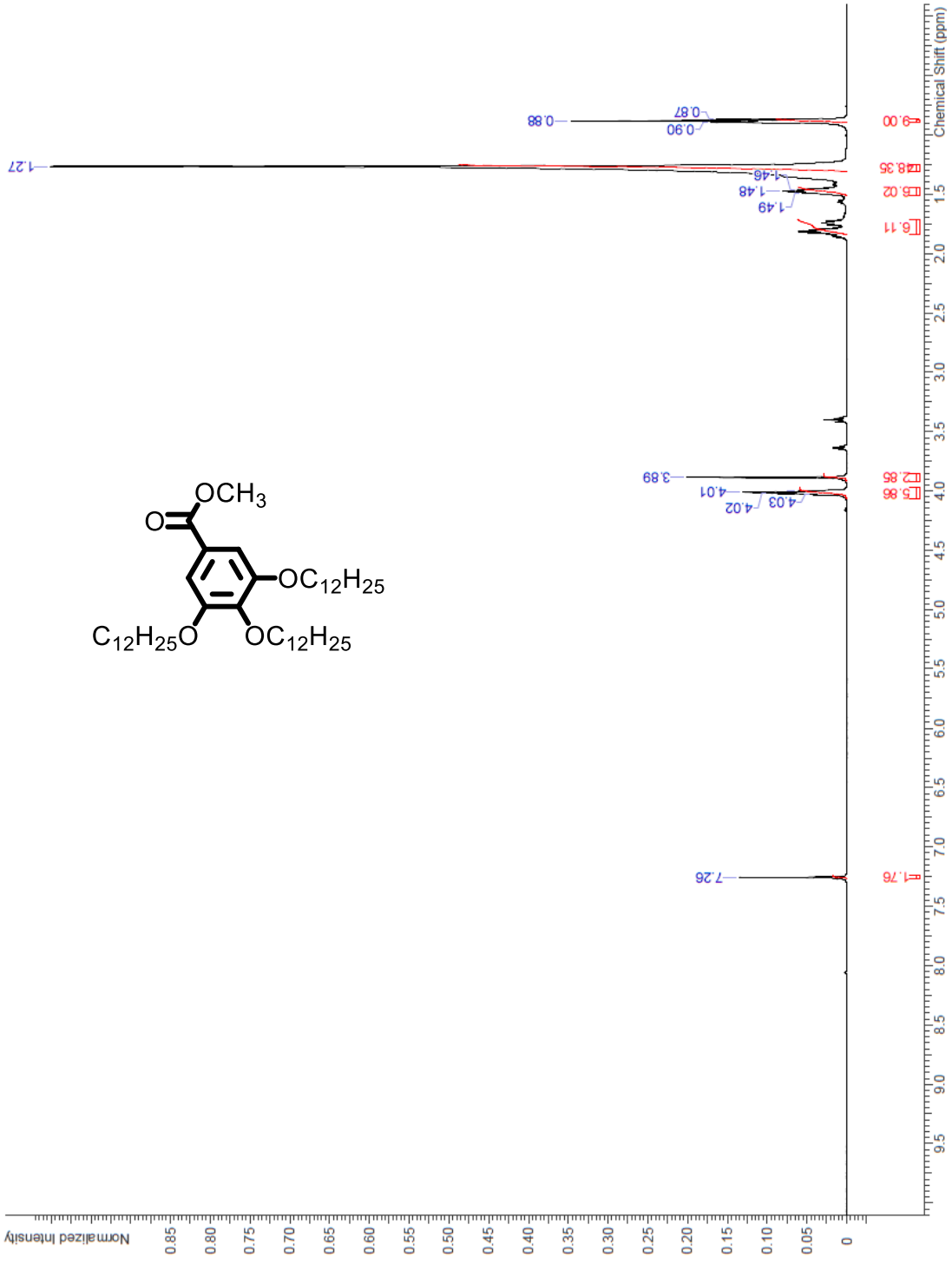
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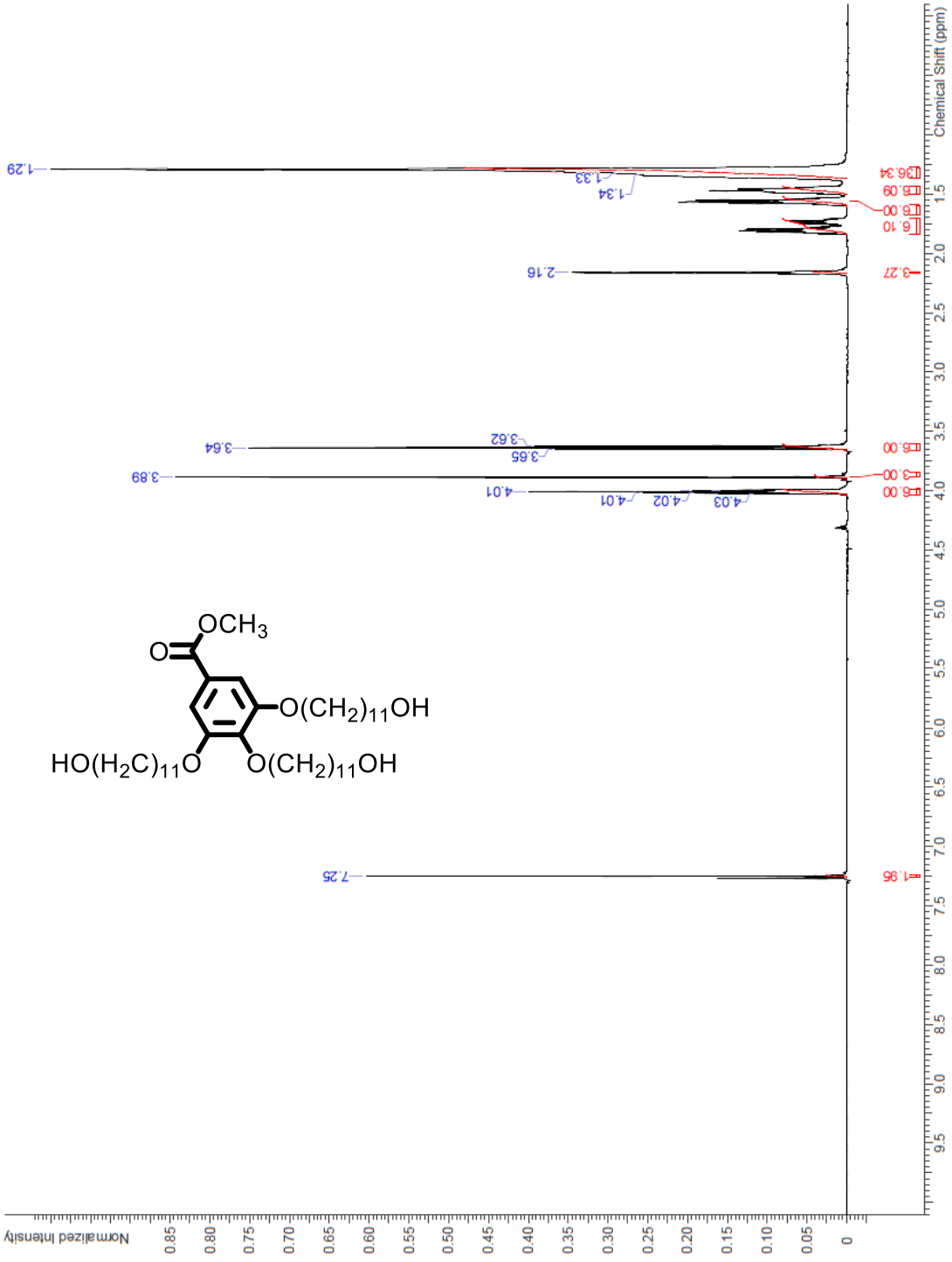
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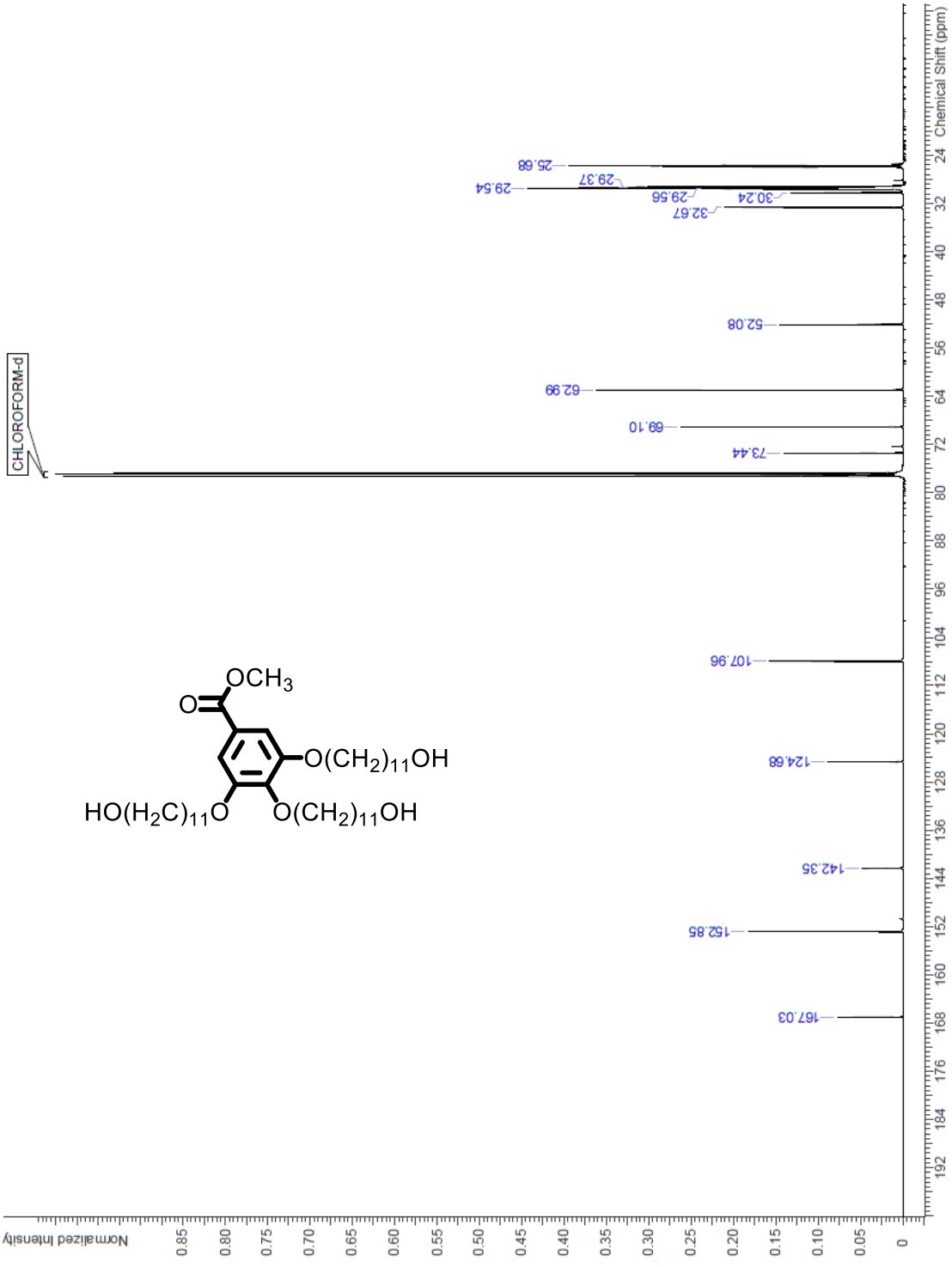
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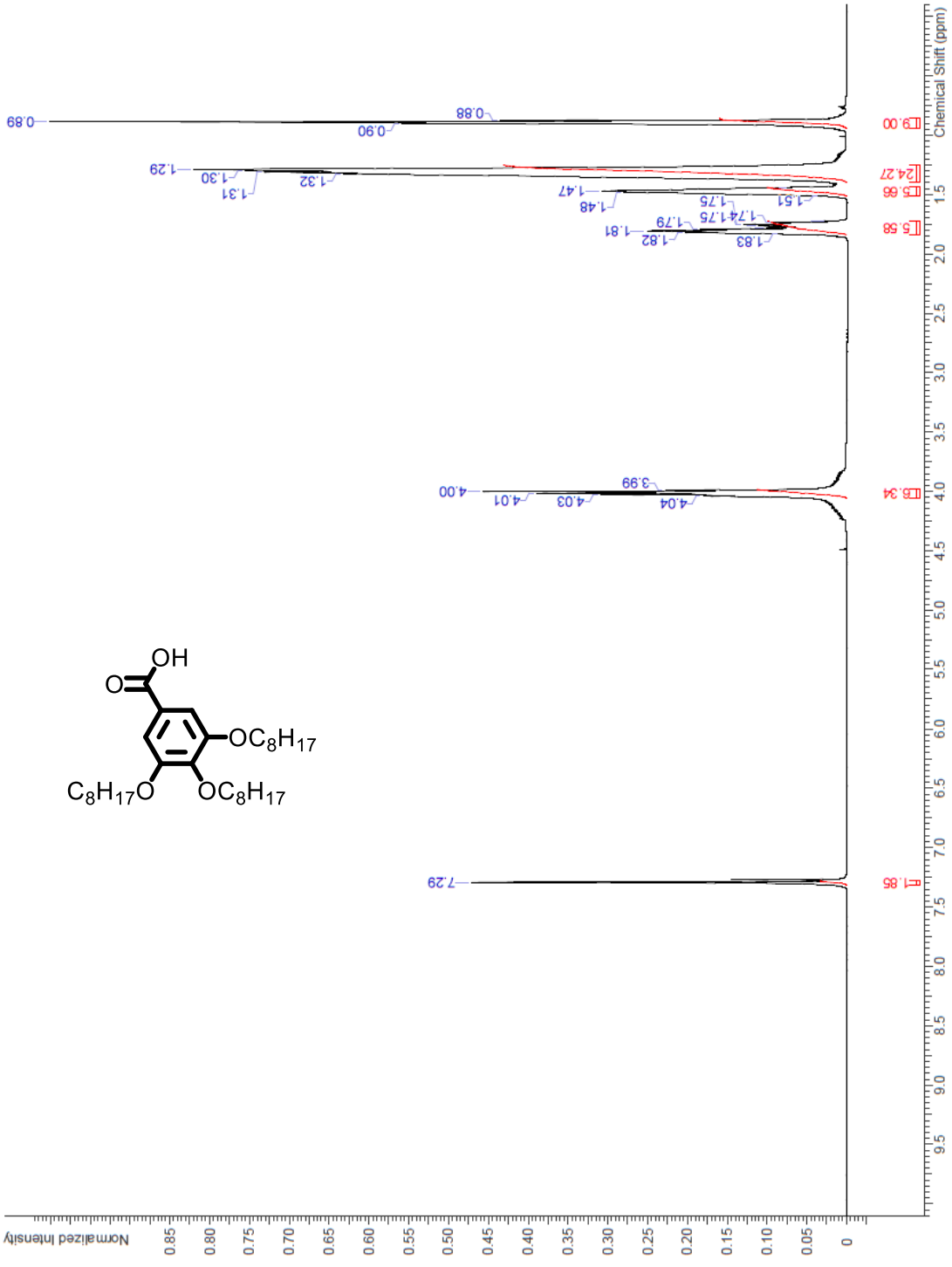
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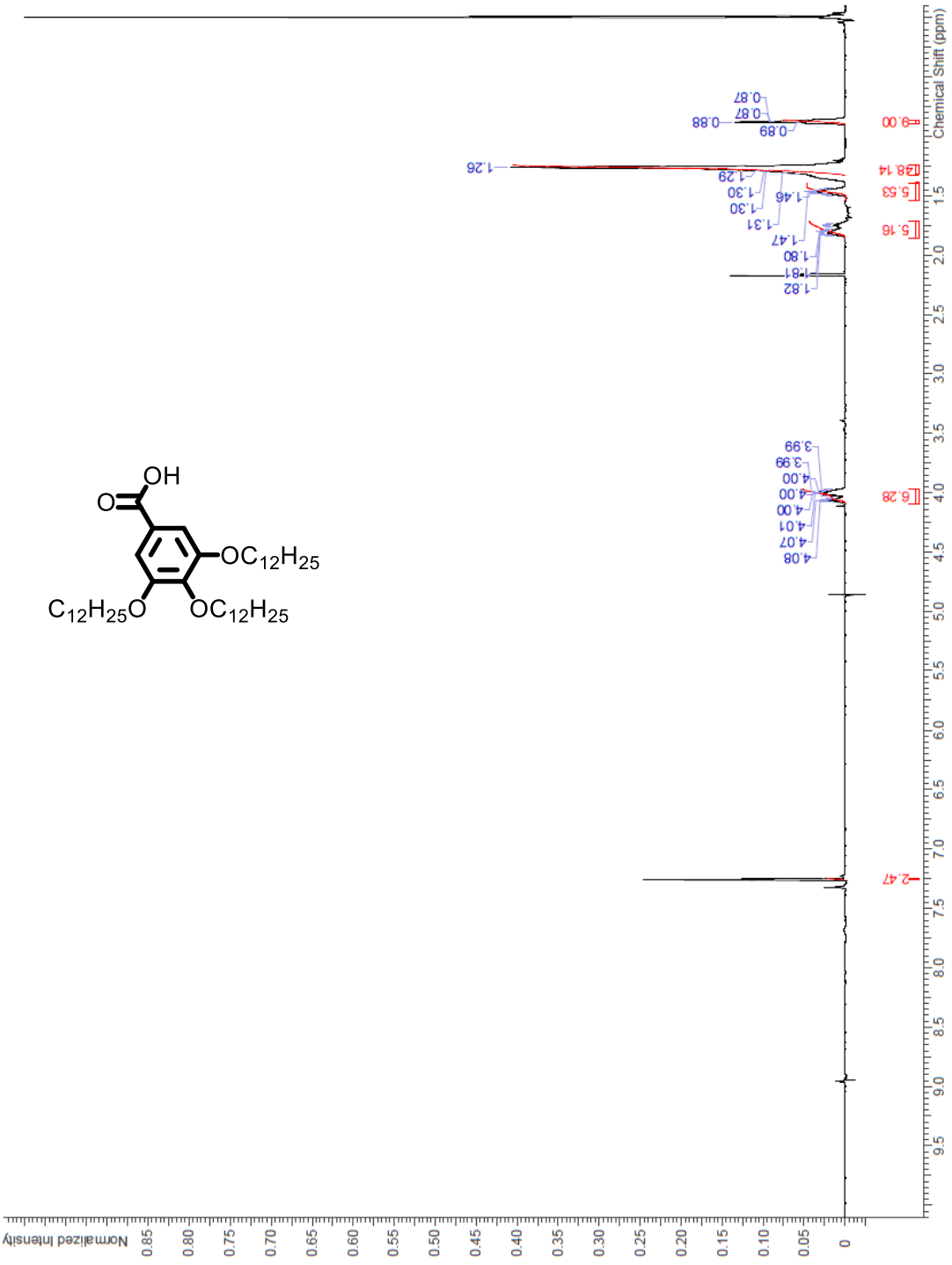
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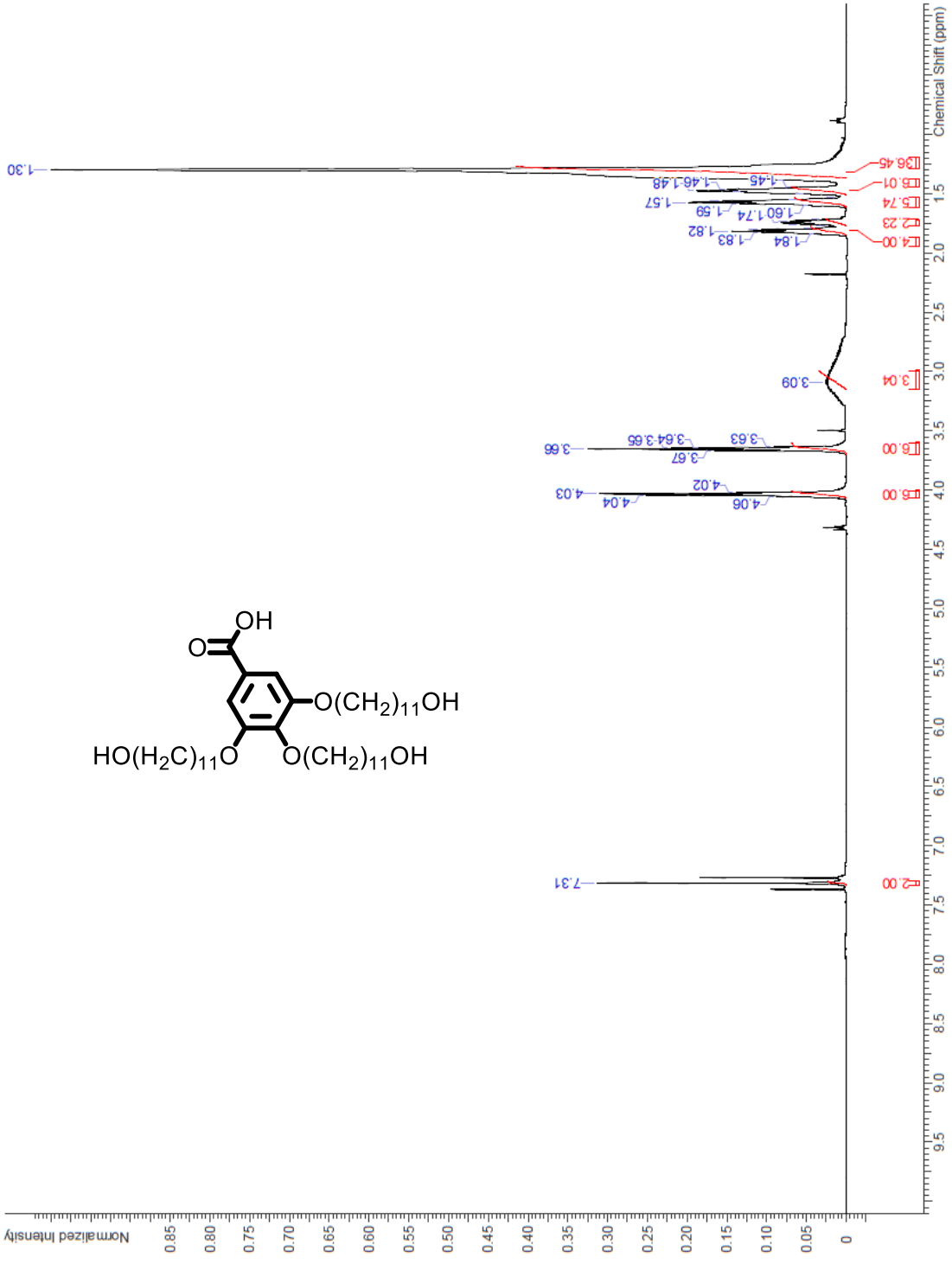
Chemical Shift (ppm)
Normalized Intensity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4.04
4.06
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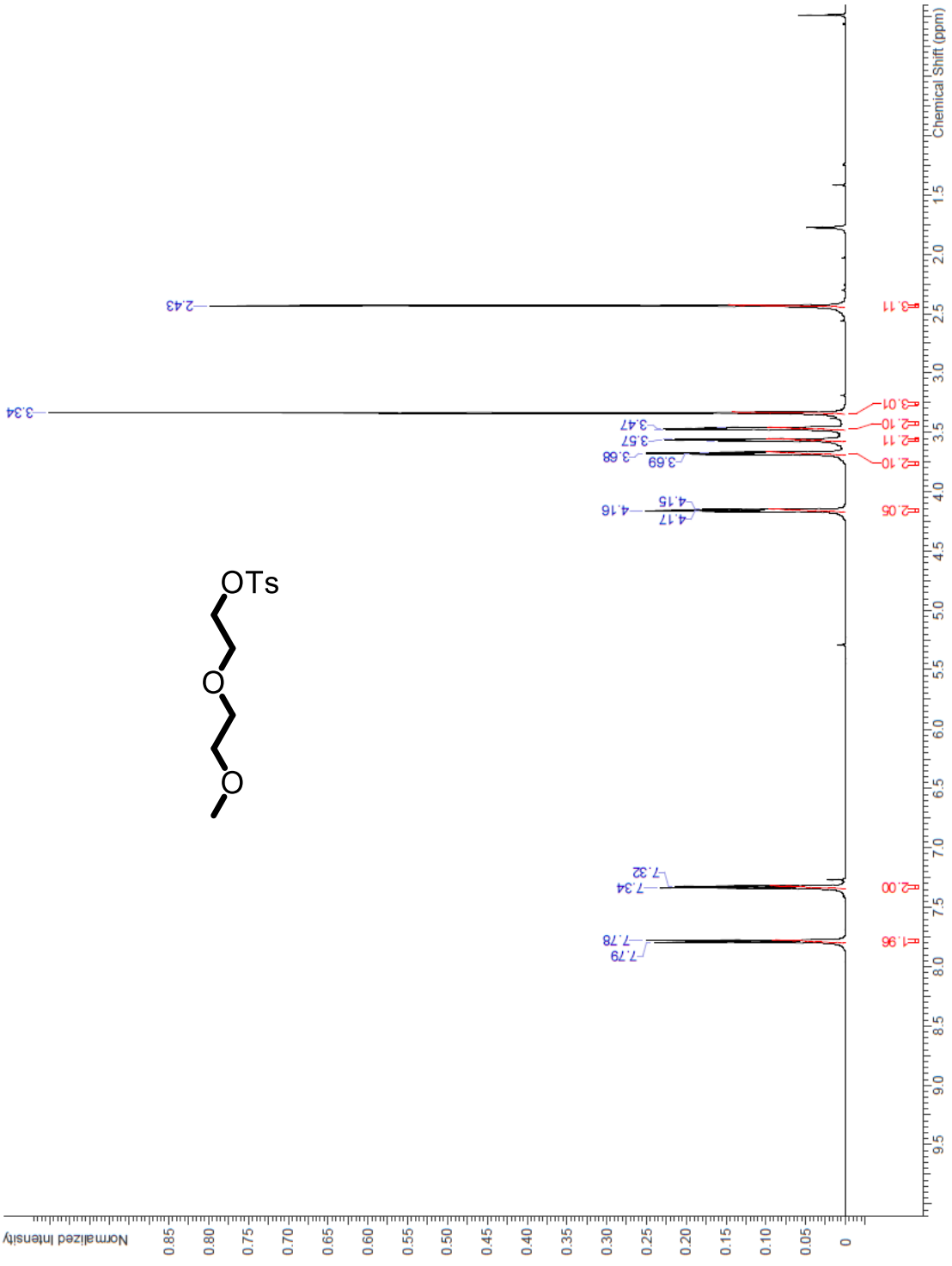
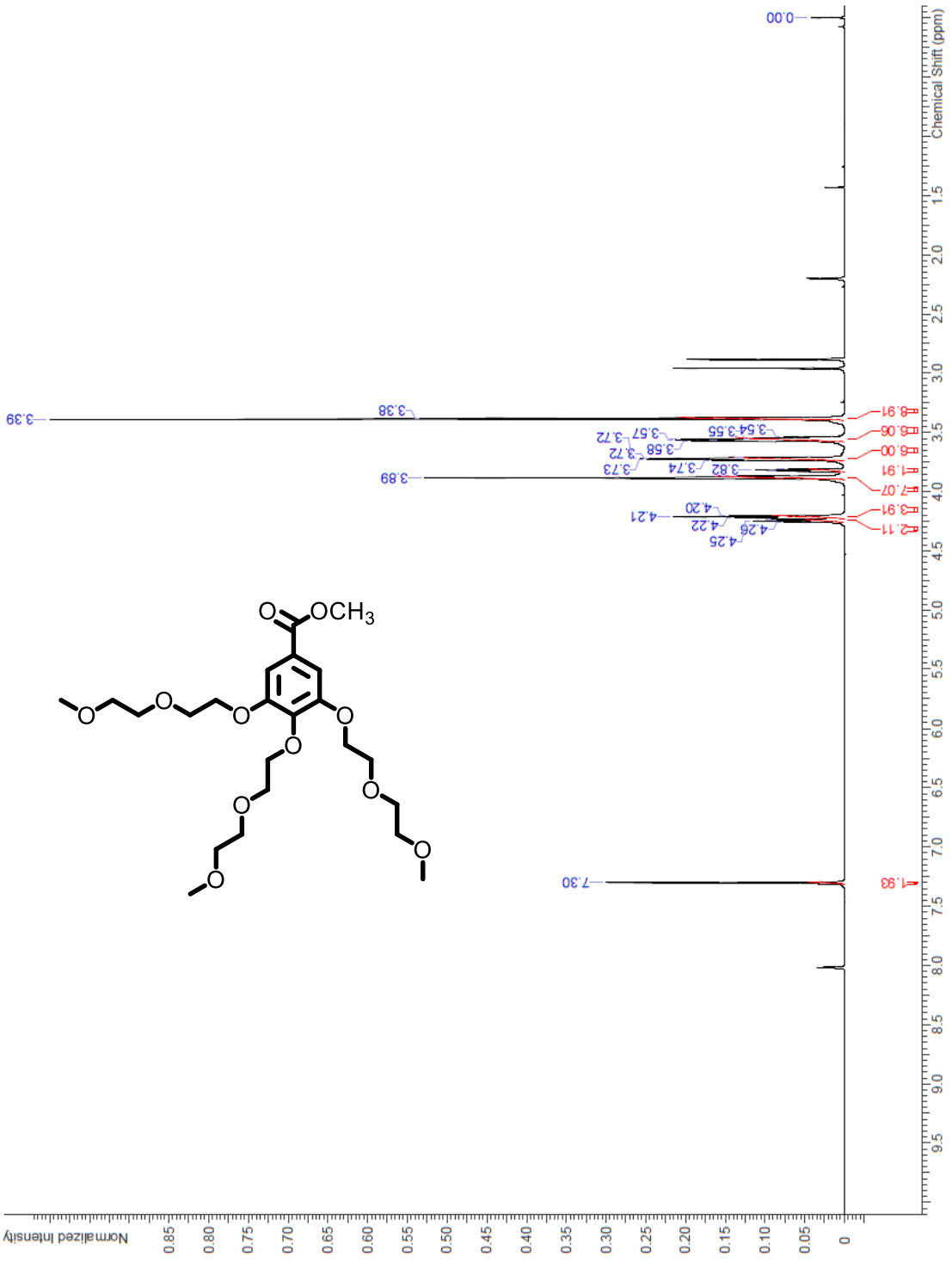
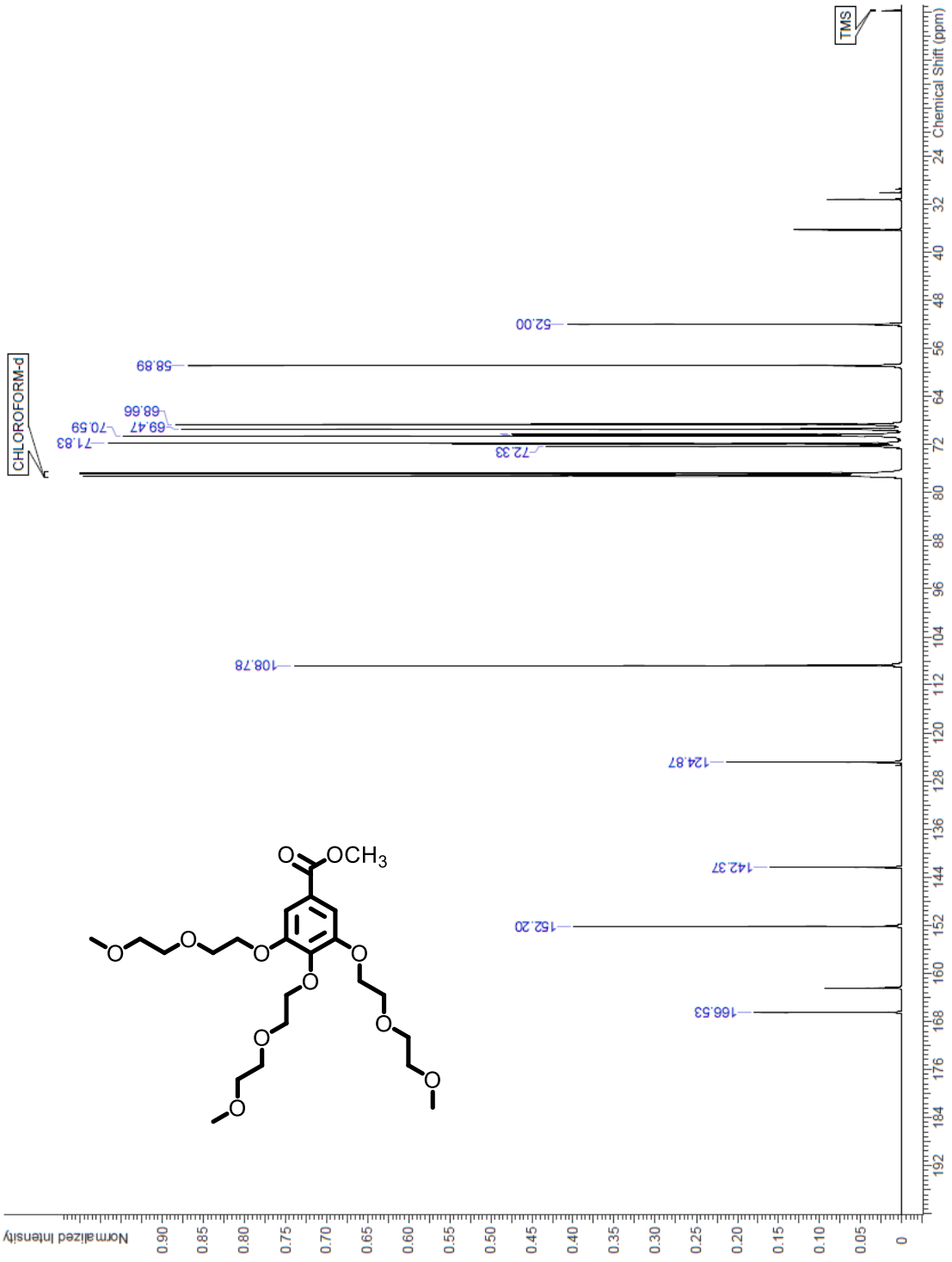
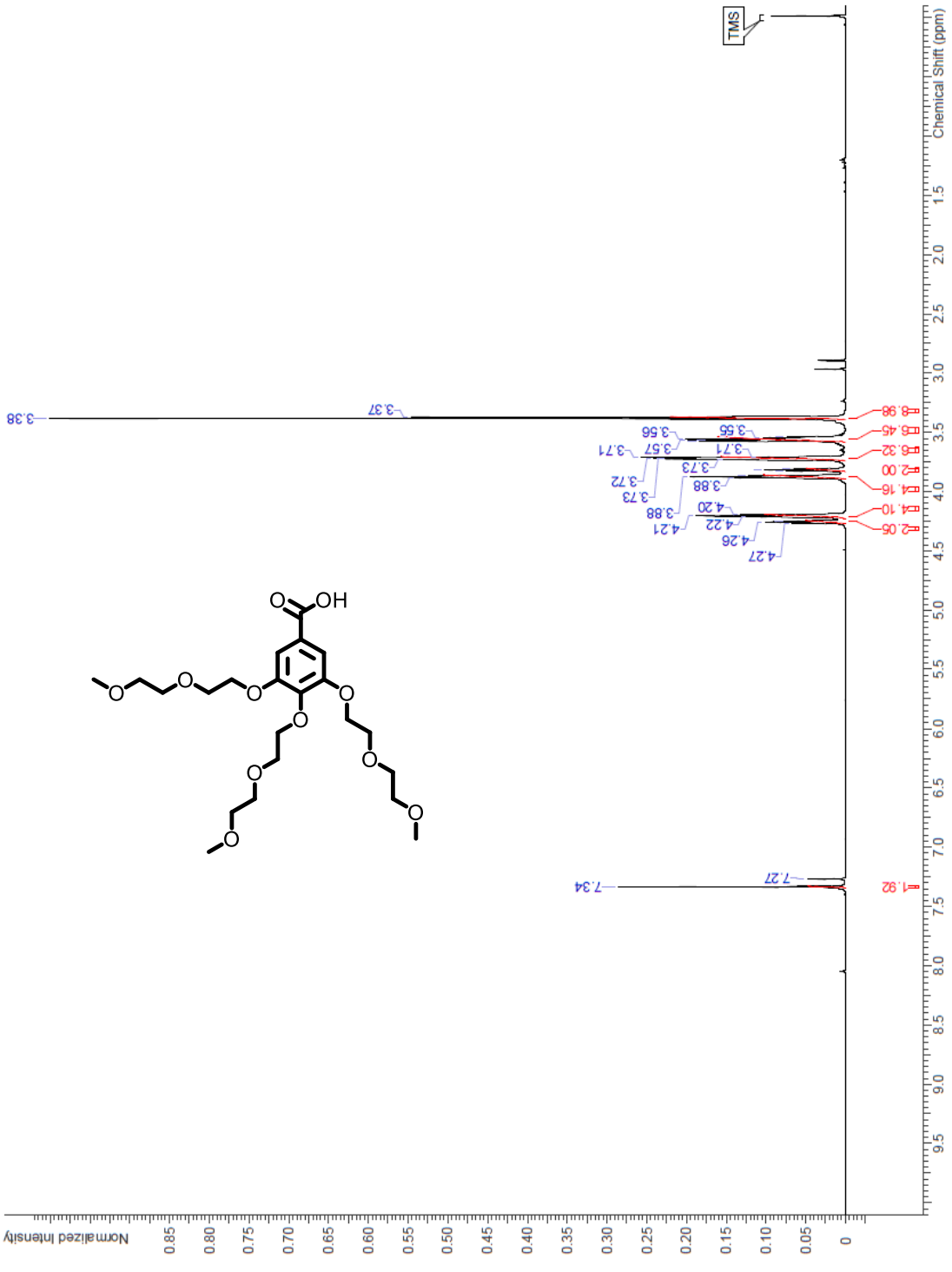
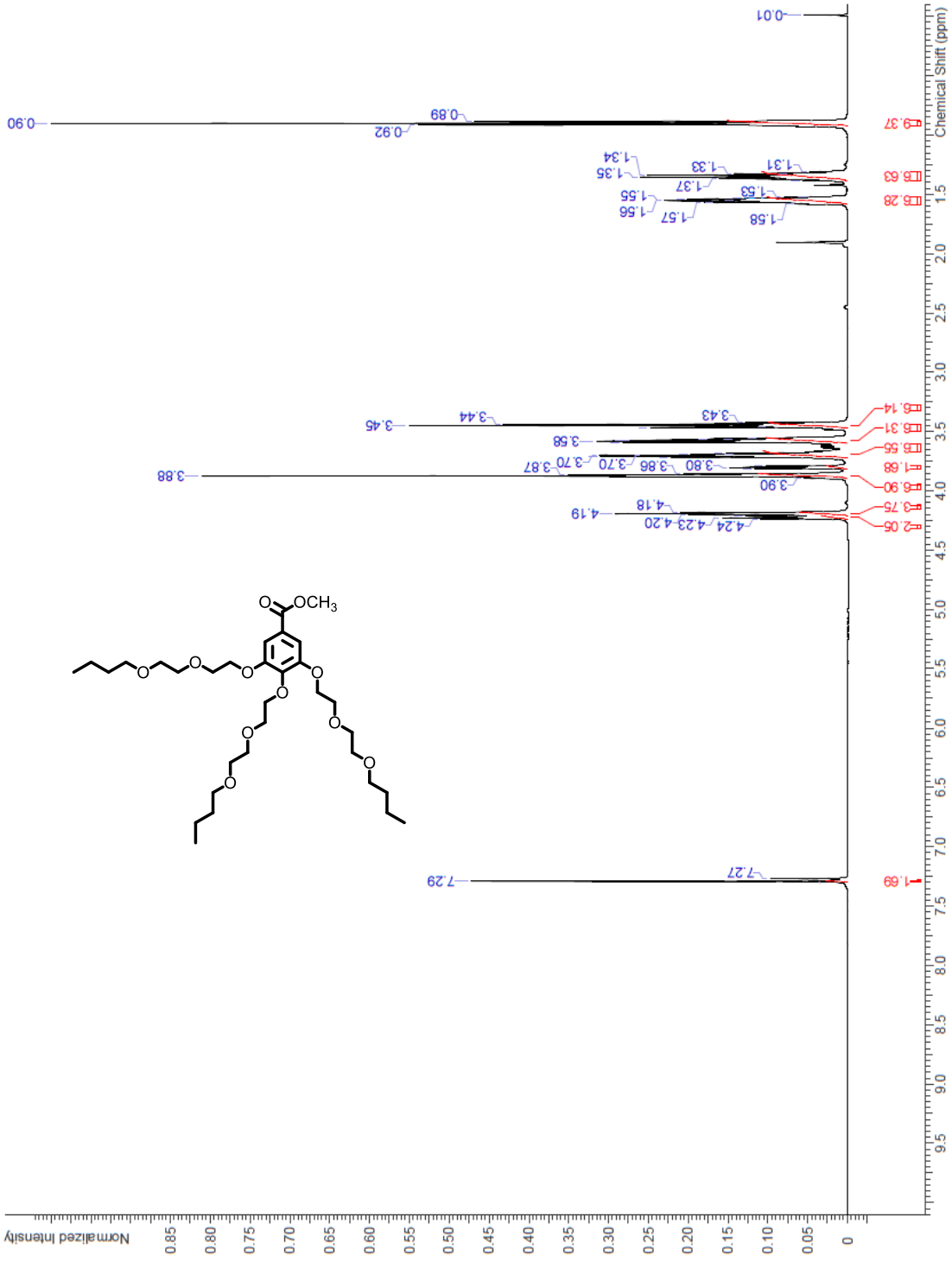
14.00
13.04
16.00
15.00
12.00

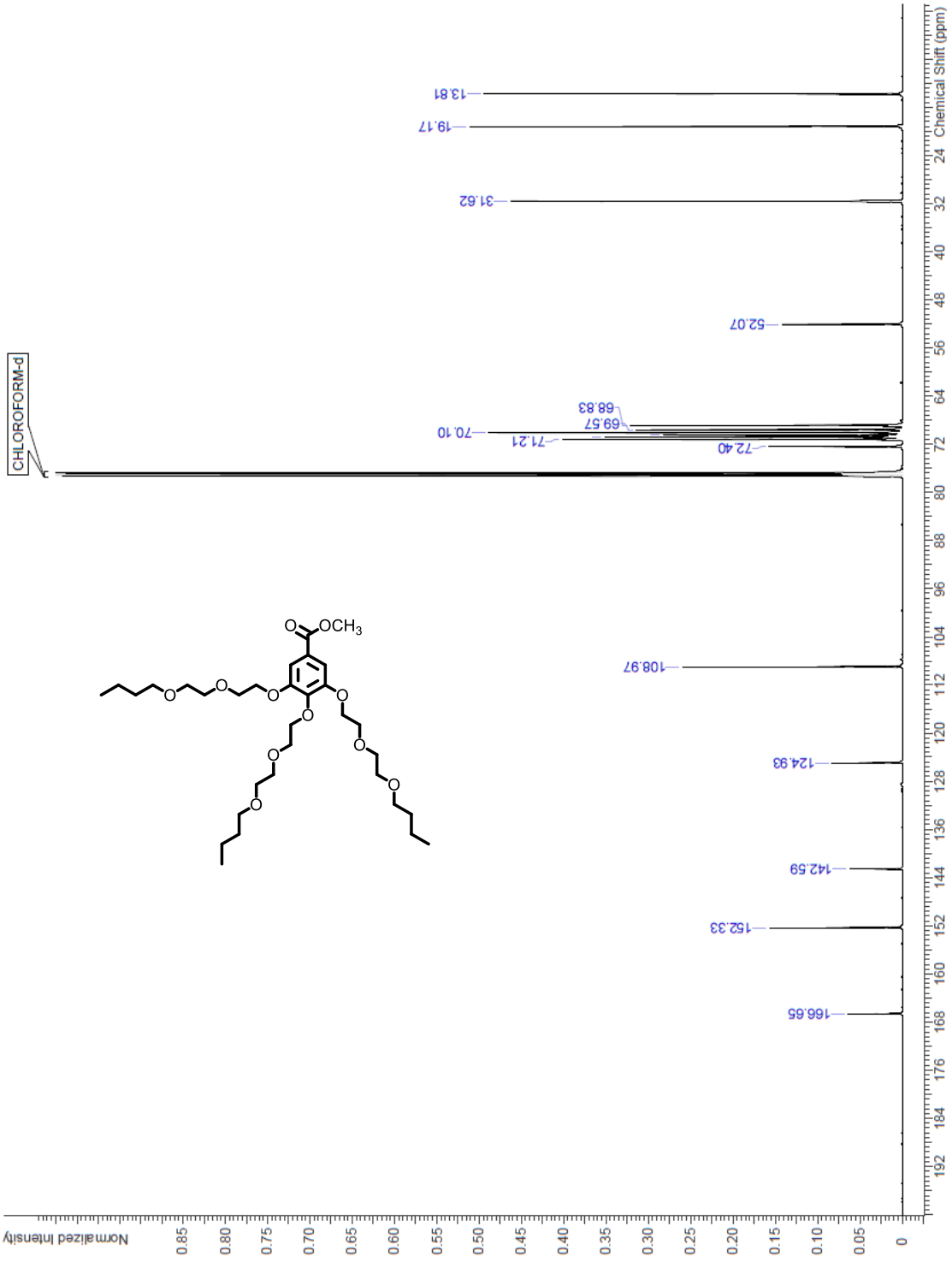

OTs
O
O
7.79
7.78
7.34
7.32
4.17
4.15
4.16
3.69
3.68
3.47
3.57
3.34
2.43
1.96
2.00
2.06
2.10
2.11
2.10
3.01
3.11
Chemical Shift (ppm)
Normalized Intensity

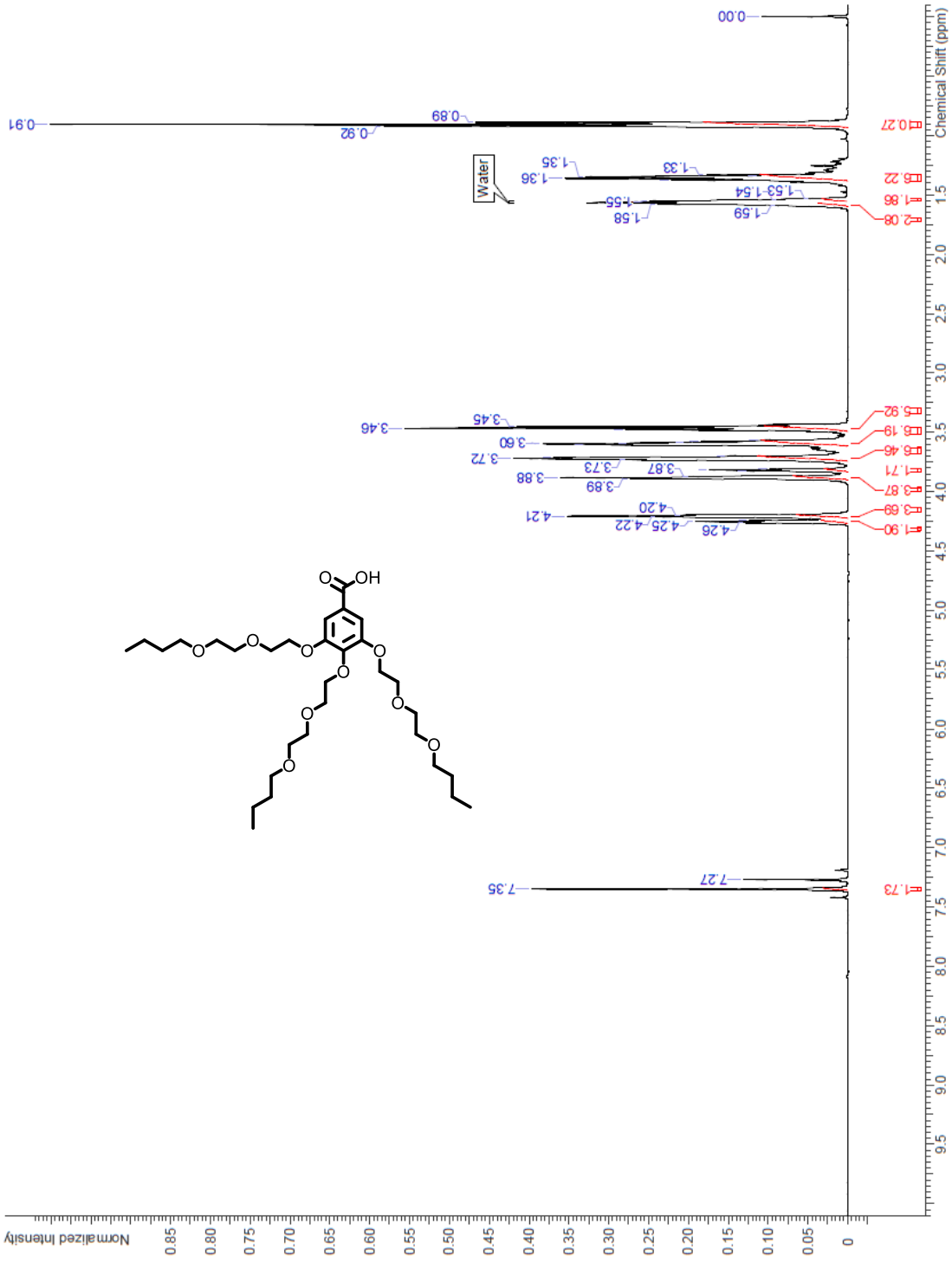

Chemical Shift (ppm)
Normalized Intensity
0.00
3.39
3.38
3.89
4.21
7.30
1.93
8.91
6.06
6.00
1.91
7.07
3.91
2.11
OCH3

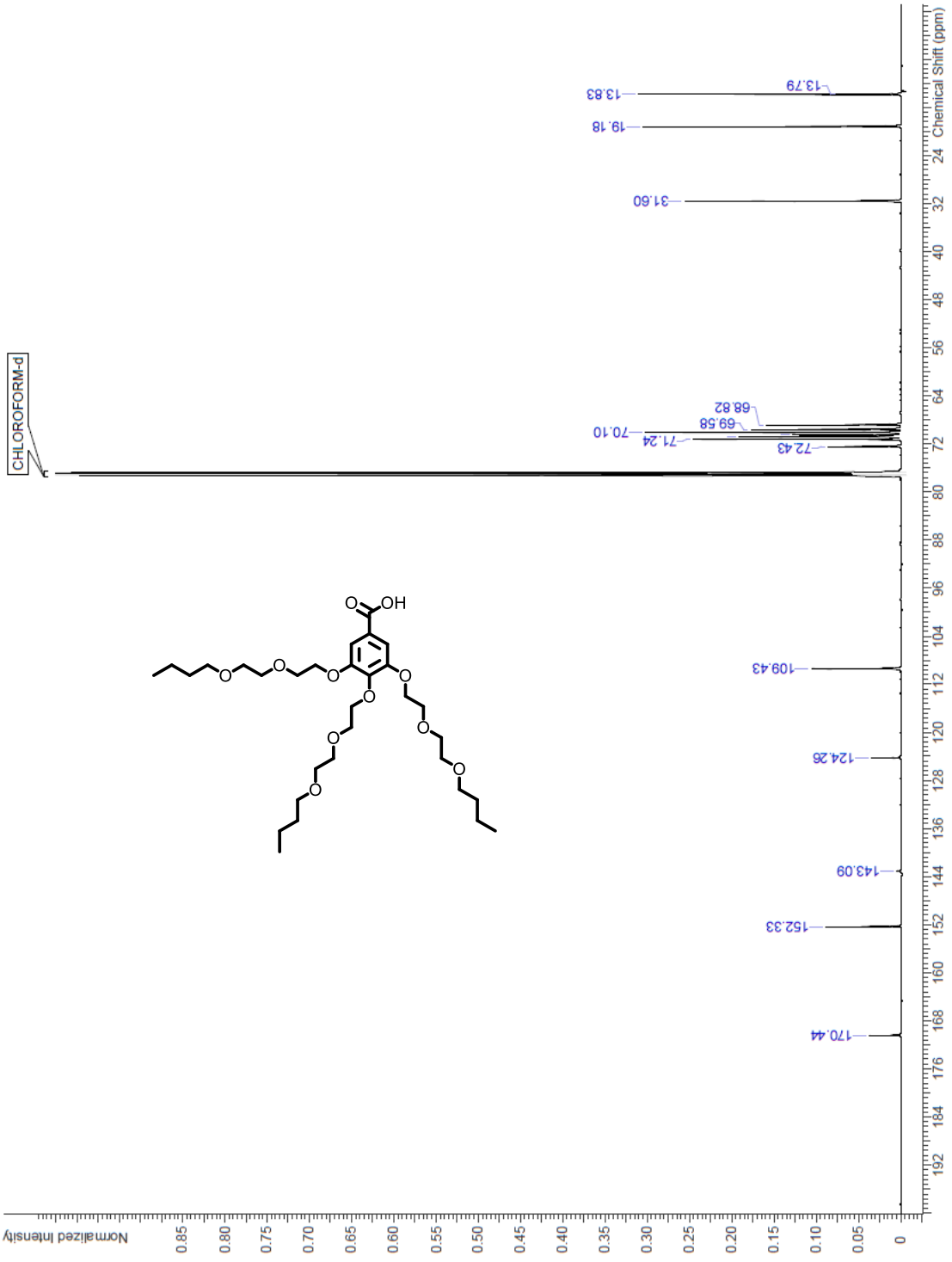

TMS
CHLOROFORM-d
166.53
152.20
142.37
124.87
108.78
72.33
71.83
70.59
69.47
68.66
58.89
52.00
Chemical Shift (ppm)
Normalized Intensity
O
OCH3

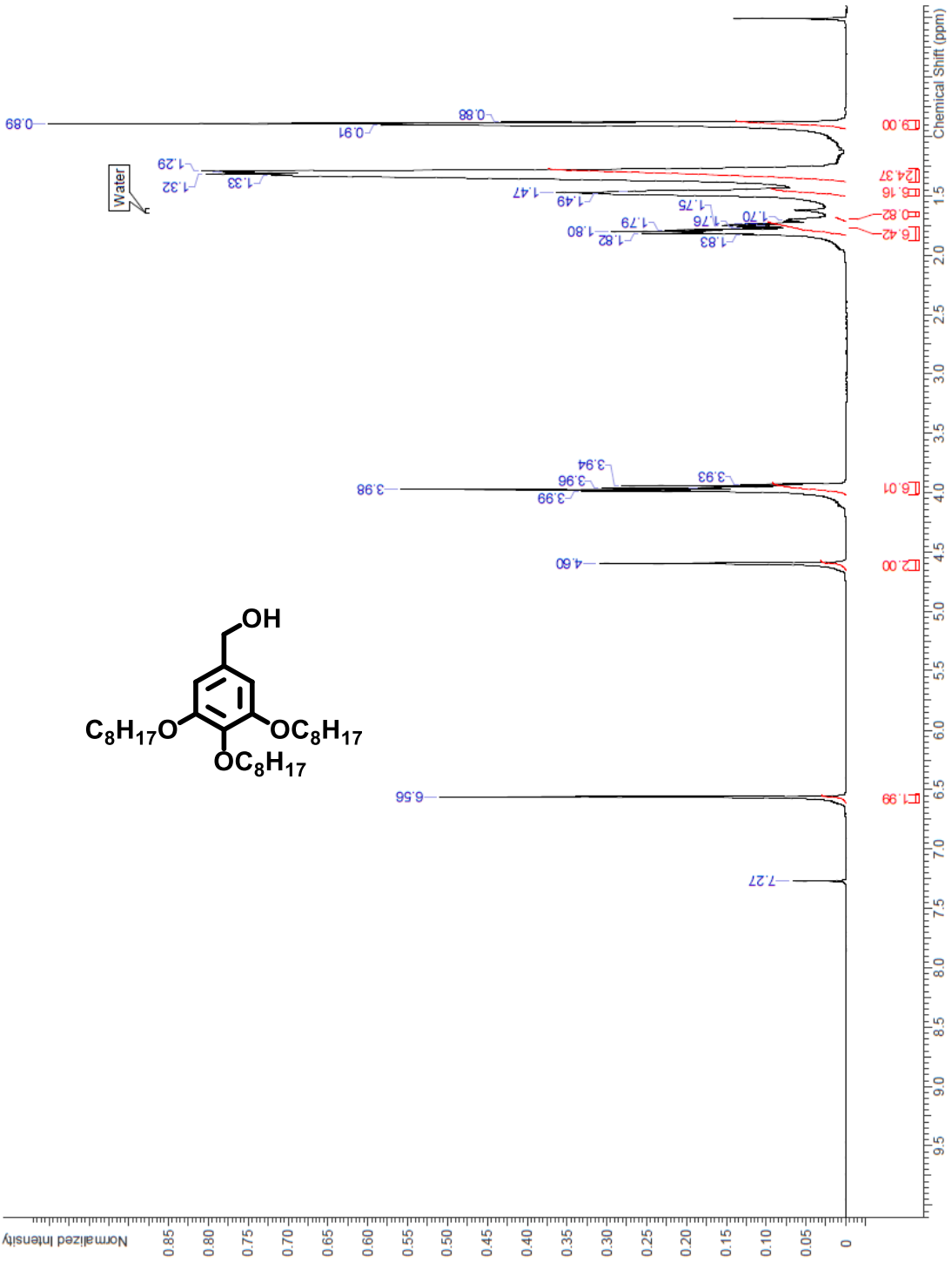

TMS
Chemical Shift (ppm)
Normalized Intensity
3.38
3.37
7.34
7.27
3.56
3.55
3.71
3.57
3.73
3.72
3.88
3.73
4.20
3.88
4.21
4.22
4.26
4.27
8.98
6.45
6.32
2.00
4.16
4.10
2.05
1.92
OH
O

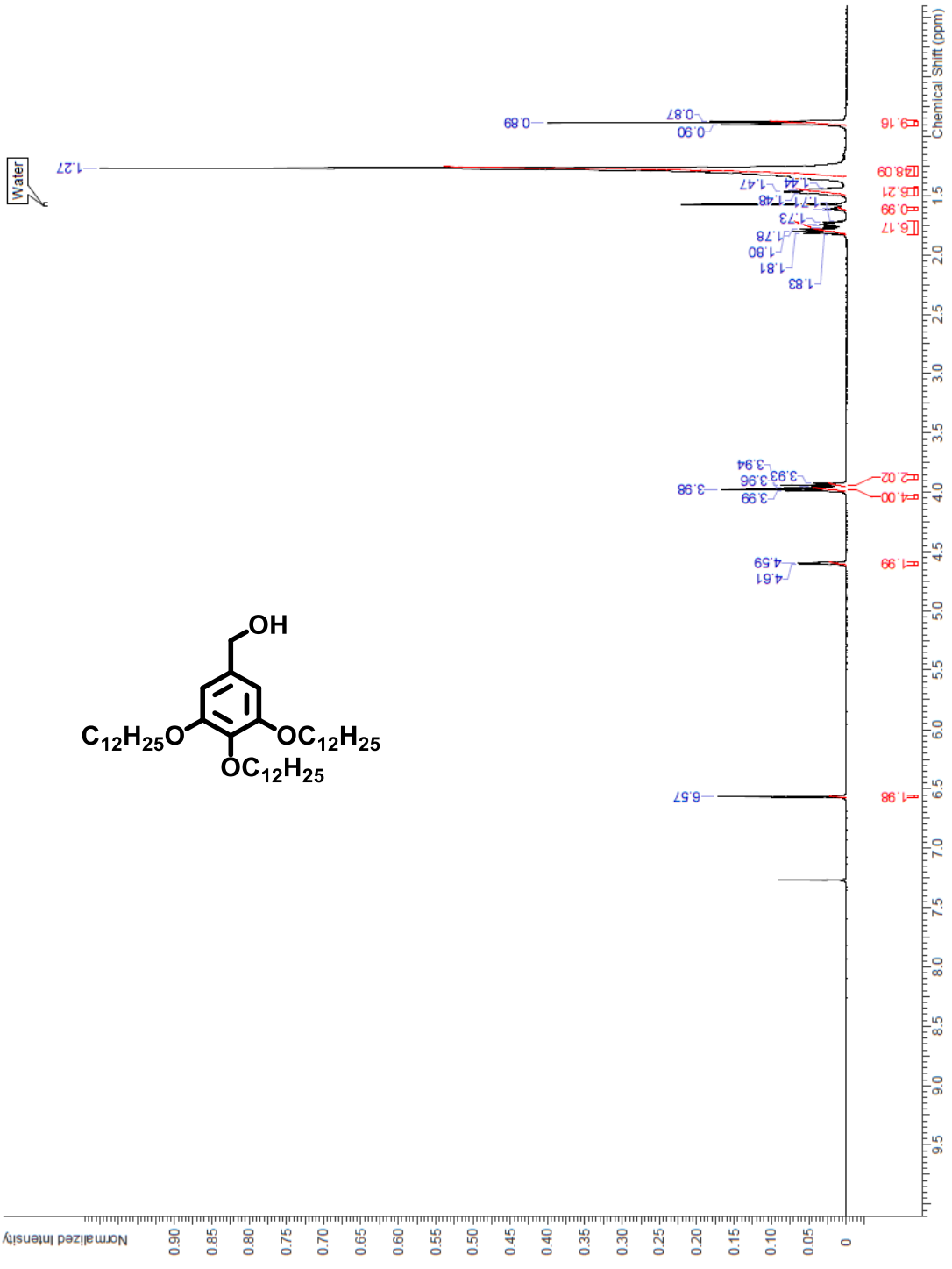

Chemical Shift (ppm)
Normalized Intensity
0.01
0.90
0.89
0.92
1.31
1.33
1.34
1.35
1.37
1.53
1.55
1.56
1.57
1.58
3.43
3.44
3.45
3.58
3.80
3.86
3.70
3.87
3.88
3.90
4.18
4.19
4.24
4.23
4.20
7.27
7.29
9.37
5.63
5.28
5.14
5.31
5.55
1.68
5.90
3.75
2.06
1.69
OCH3

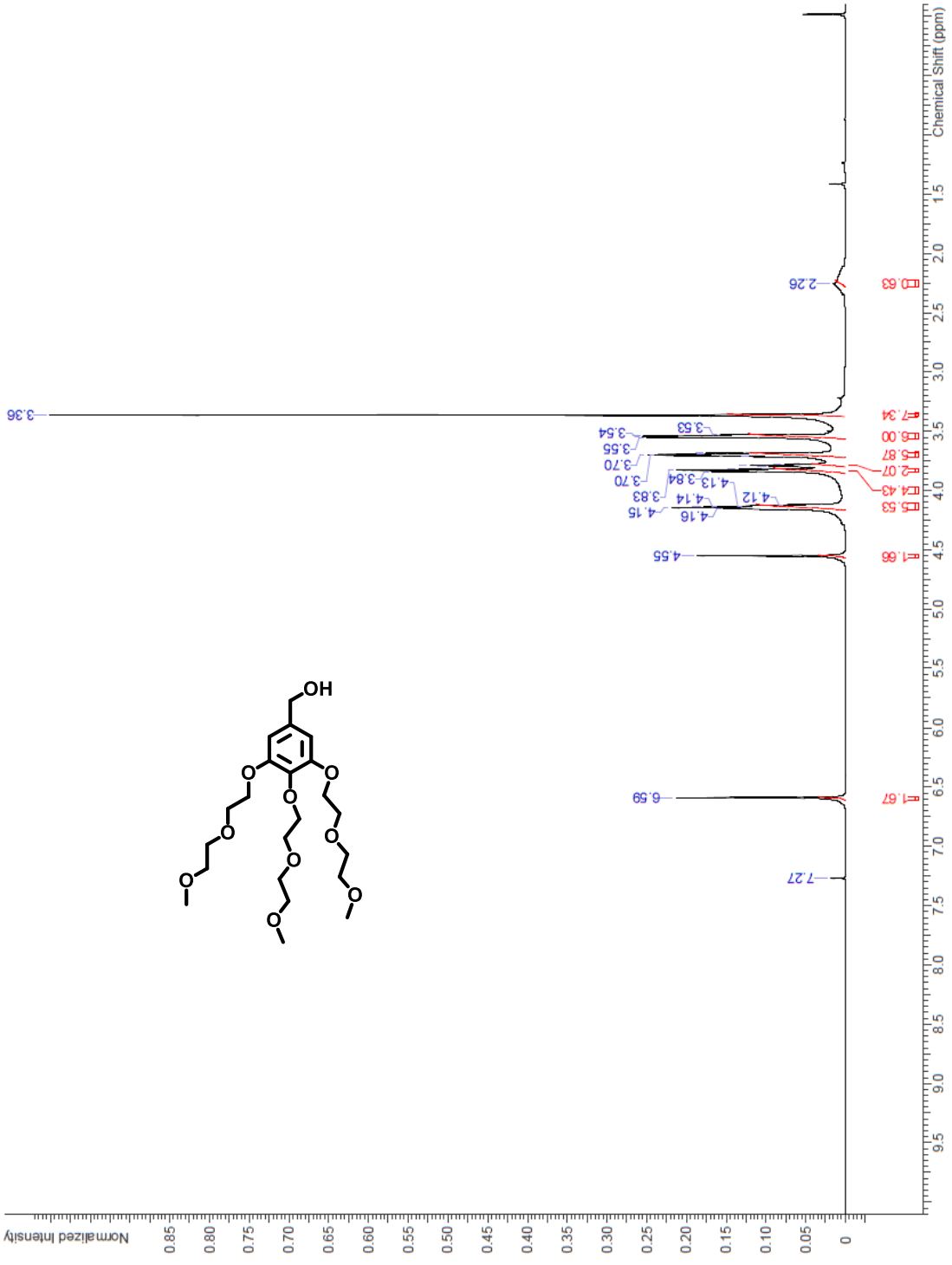

13.81
19.17
31.62
52.07
68.83
69.57
70.10
71.21
72.40
108.97
124.93
142.59
152.33
166.65
CHLOROFORM-d
Chemical Shift (ppm)
Normalized Intensity
OCH3

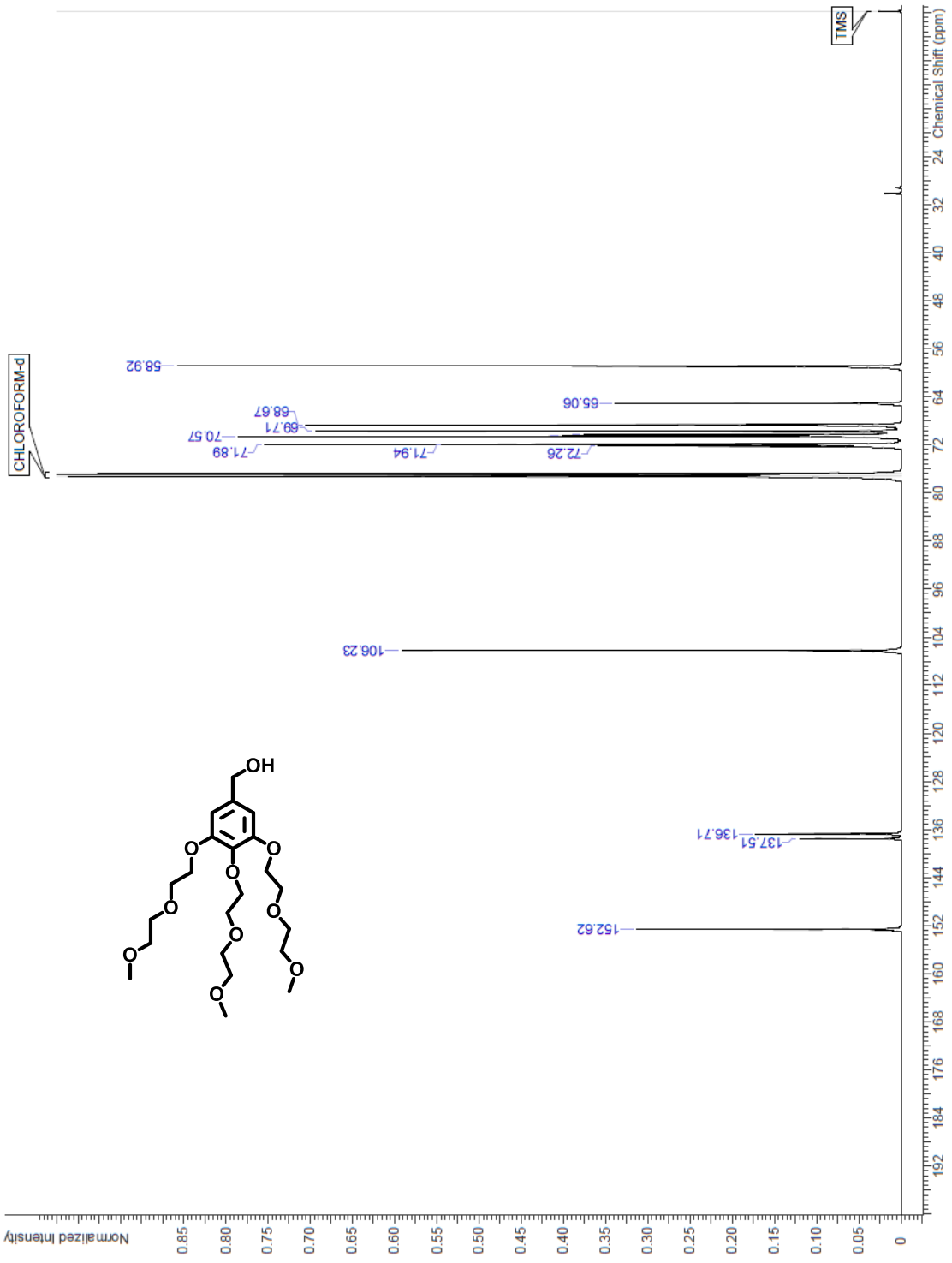

Chemical Shift (ppm)
Normalized Intensity
Water
0.00
0.89
0.92
0.91
1.33
1.35
1.36
1.53-1.54
1.55
1.58
1.59
3.45
3.46
3.60
3.72
3.73
3.87
3.88
3.89
4.20
4.21
4.22
4.25
4.26
7.27
7.35
OH

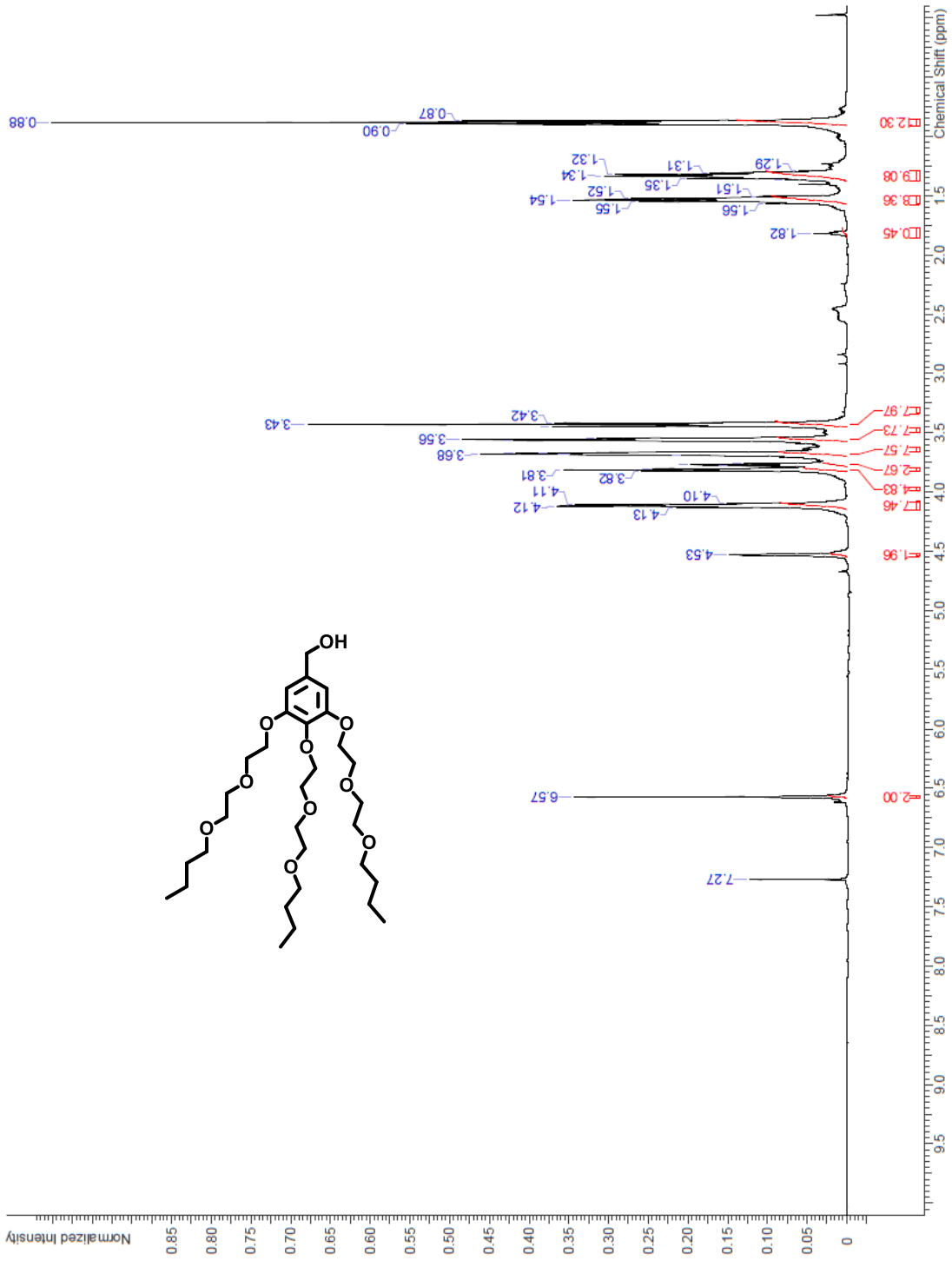

CHLOROFORM-d
13.79
13.83
19.18
31.60
68.82
69.58
70.10
71.24
72.43
109.43
124.26
143.09
152.33
170.44
Chemical Shift (ppm)
Normalized Intensity
OH
O

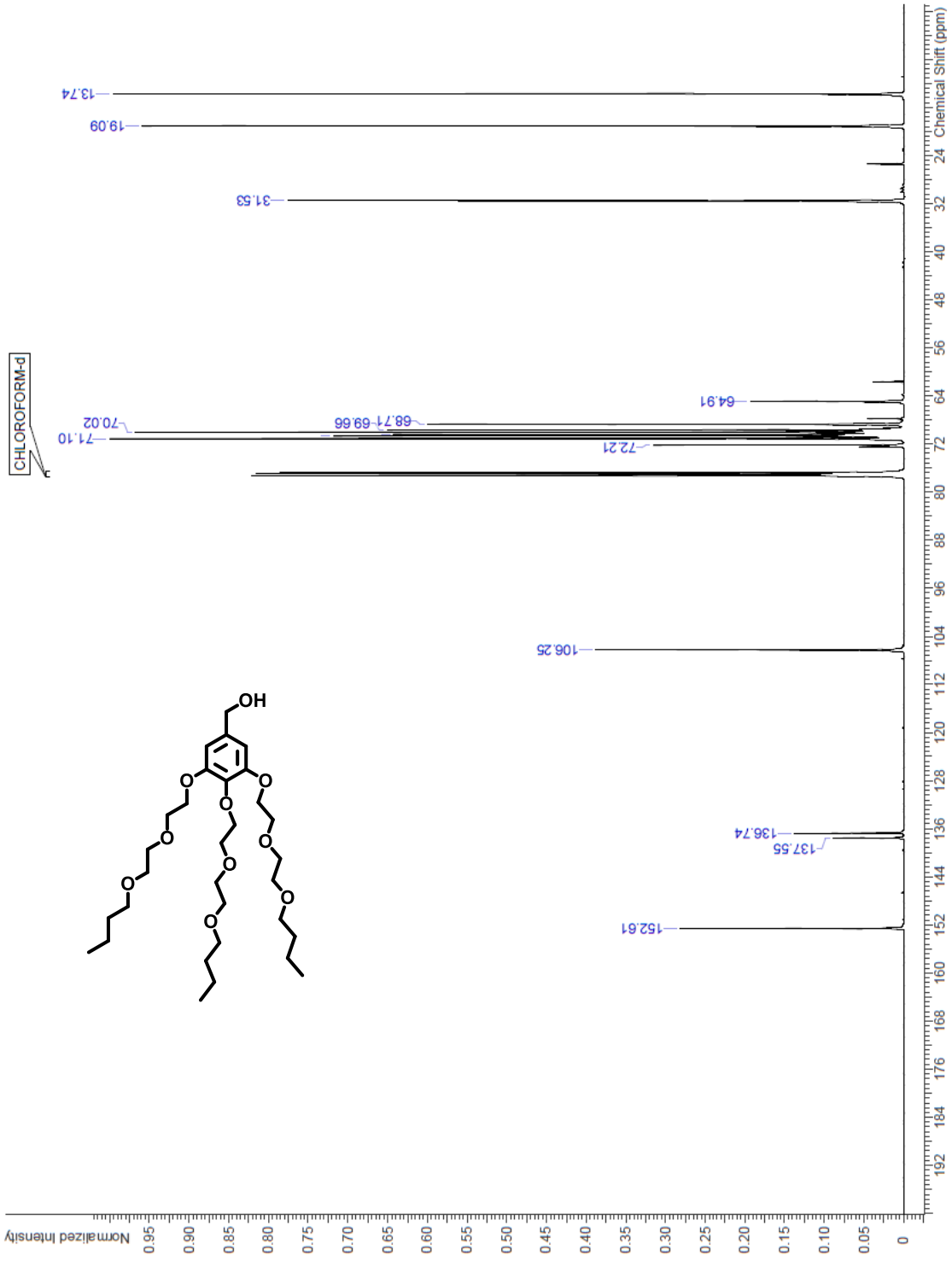

OH
C8H17O
OC8H17
OC8H17
Water
0.89
0.91
0.88
1.29
1.32
1.33
1.47
1.49
1.75
1.76
1.79
1.80
1.82
1.83
3.93
3.94
3.96
3.99
3.98
4.60
6.56
7.27
9.00
24.37
5.16
0.82
6.42
6.01
2.00
1.99
Chemical Shift (ppm)
Normalized Intensity

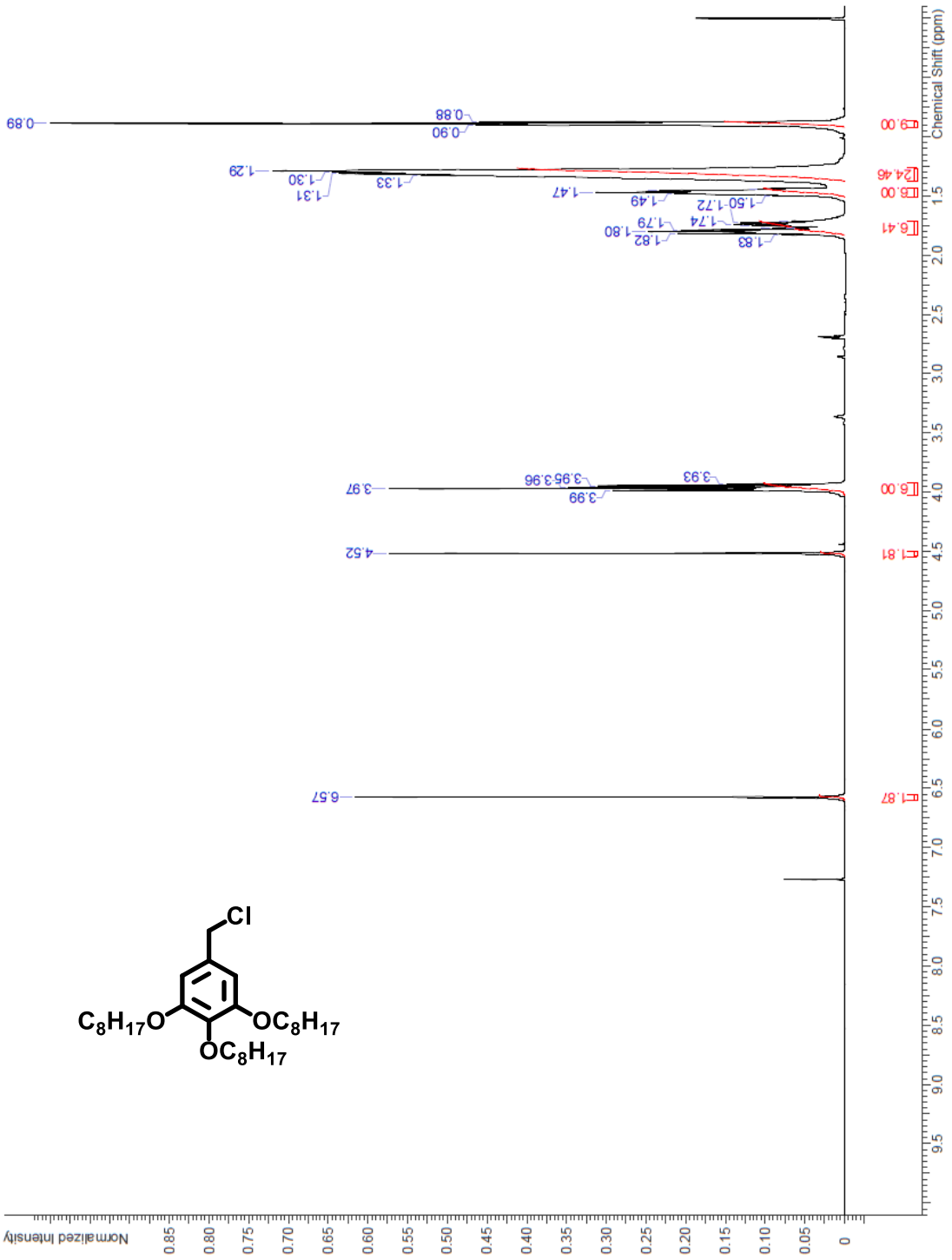

Water
1.27
0.89
0.87
0.90
1.44
1.47
1.48
1.73
1.78
1.80
1.81
1.83
3.93
3.94
3.96
3.98
3.99
4.59
4.61
6.57
9.16
28.09
15.21
0.99
6.17
2.02
4.00
1.99
1.98
Chemical Shift (ppm)
Normalized Intensity
OH
C12H25O
OC12H25
OC12H25

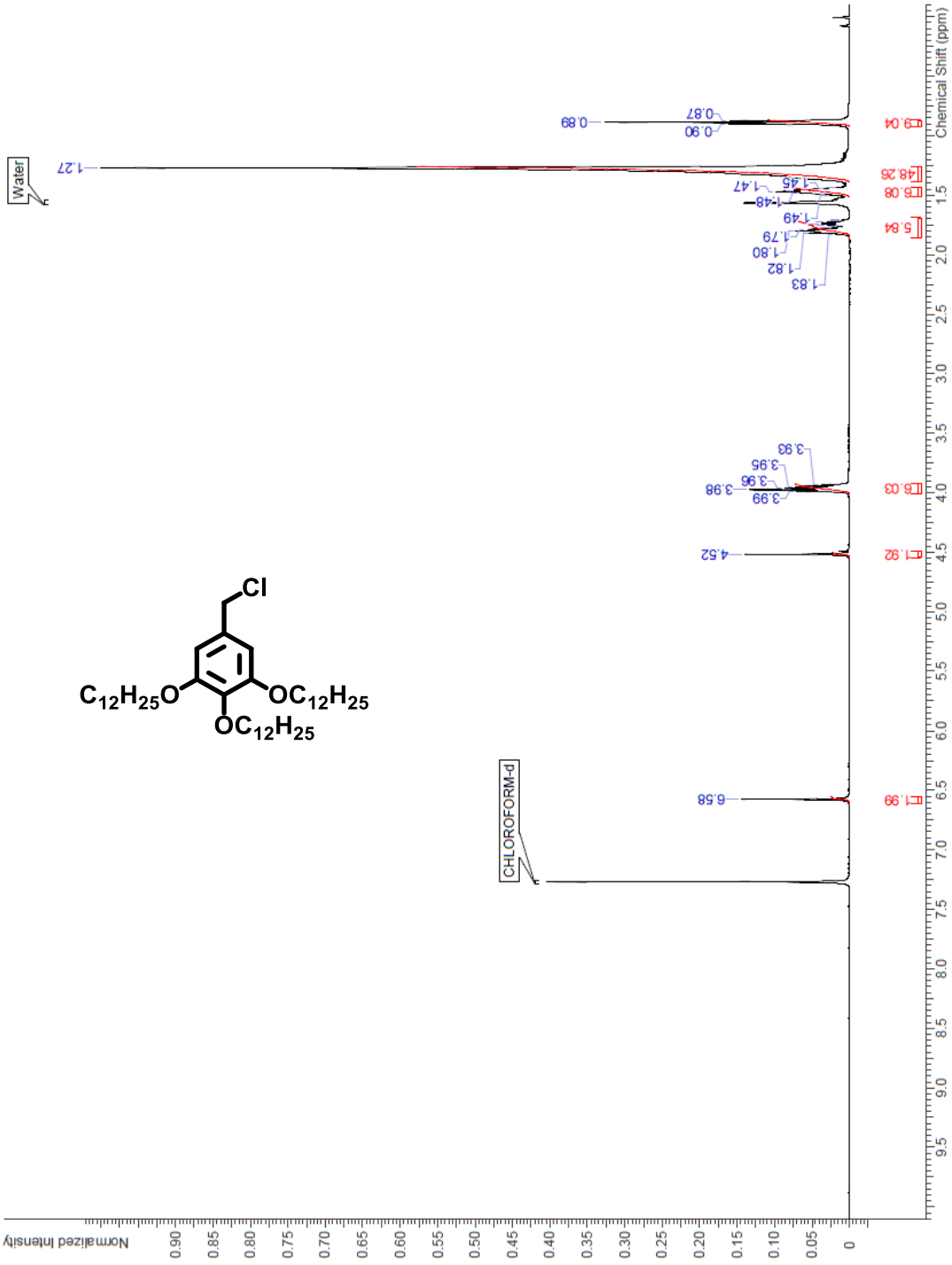

Chemical Shift (ppm)
Normalized Intensity
OH
O
2.26
3.36
3.53
3.54
3.55
3.70
3.70
4.13
3.84
4.12
4.14
3.83
4.15
4.16
4.55
6.59
7.27

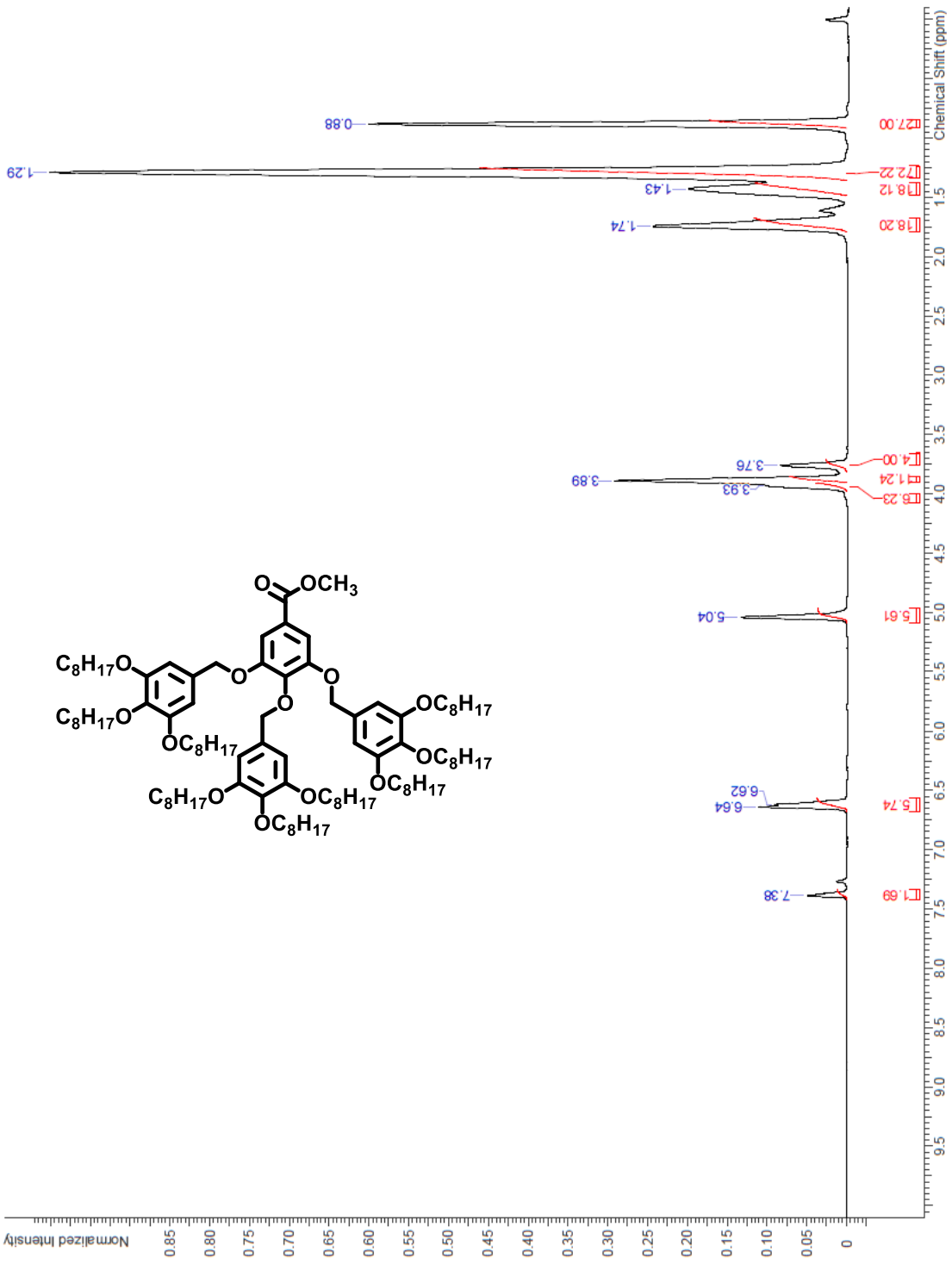

TMS
CHLOROFORM-d
58.92
65.06
68.67
69.71
70.57
71.89
71.94
72.26
106.23
136.71
137.51
152.62
OH
Chemical Shift (ppm)
Normalized Intensity

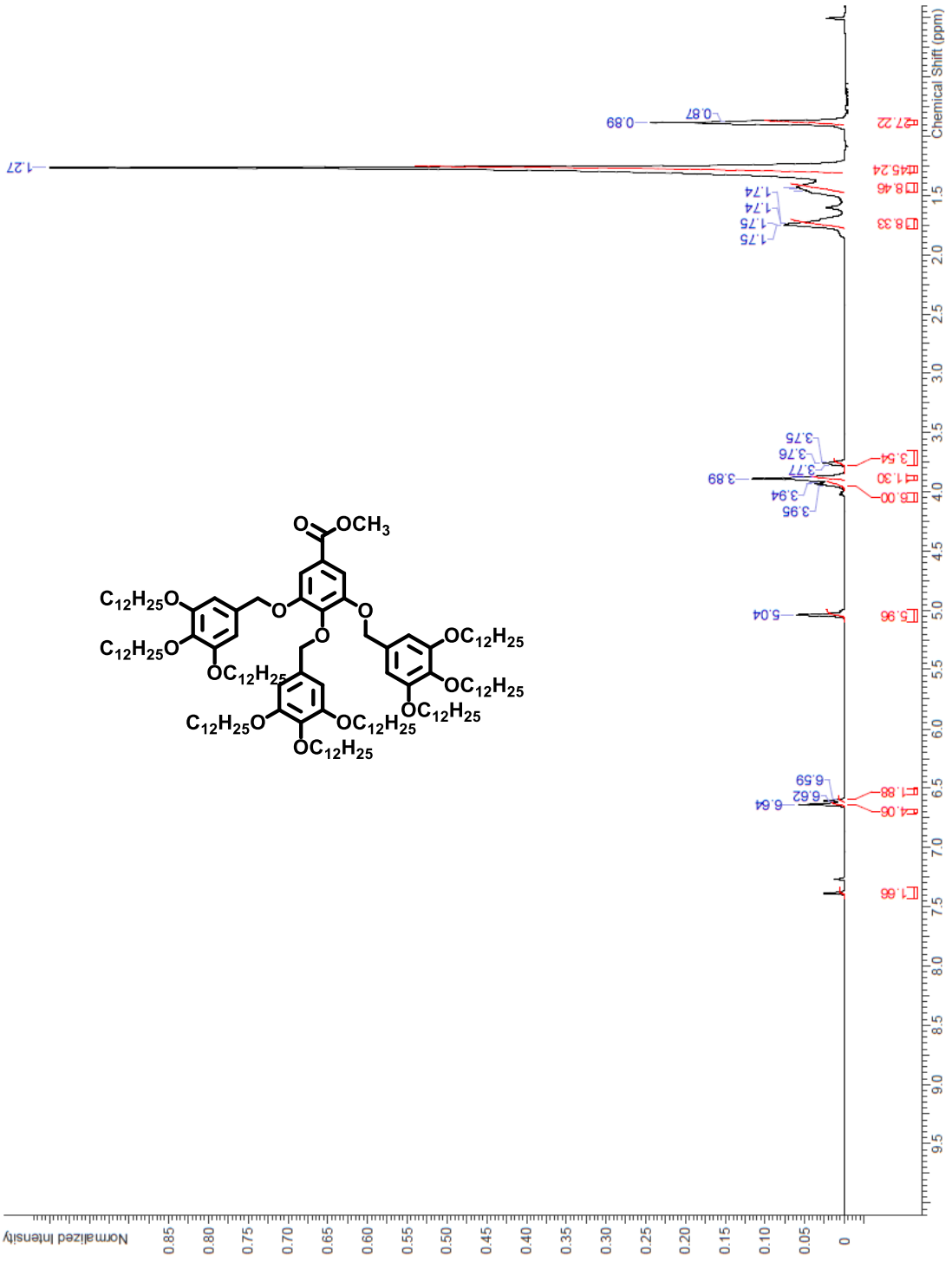

Chemical Shift (ppm)
Normalized Intensity
OH
O
0.88
0.87
0.90
1.29
1.31
1.32
1.34
1.35
1.51
1.52
1.54
1.55
1.56
1.82
3.42
3.43
3.56
3.68
3.81
3.82
4.10
4.11
4.12
4.13
4.53
6.57
7.27
2.30
9.08
8.36
0.45
7.97
7.73
7.57
2.67
4.83
7.46
1.96
2.00

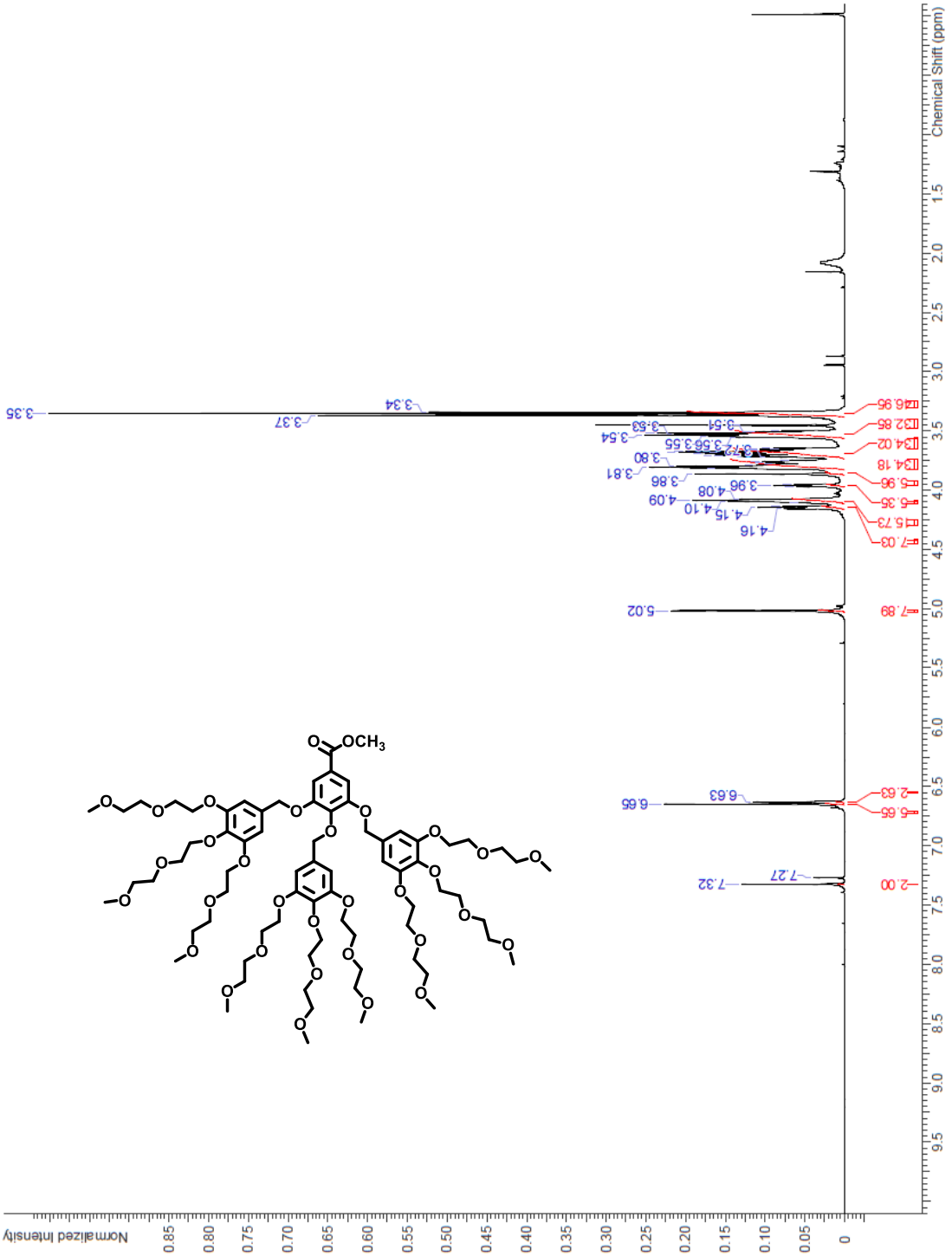

13.74
19.09
31.53
64.91
68.71-69.66
70.02
71.10
72.21
106.25
136.74
137.55
152.61
CHLOROFORM-d
OH
Chemical Shift (ppm)
Normalized Intensity

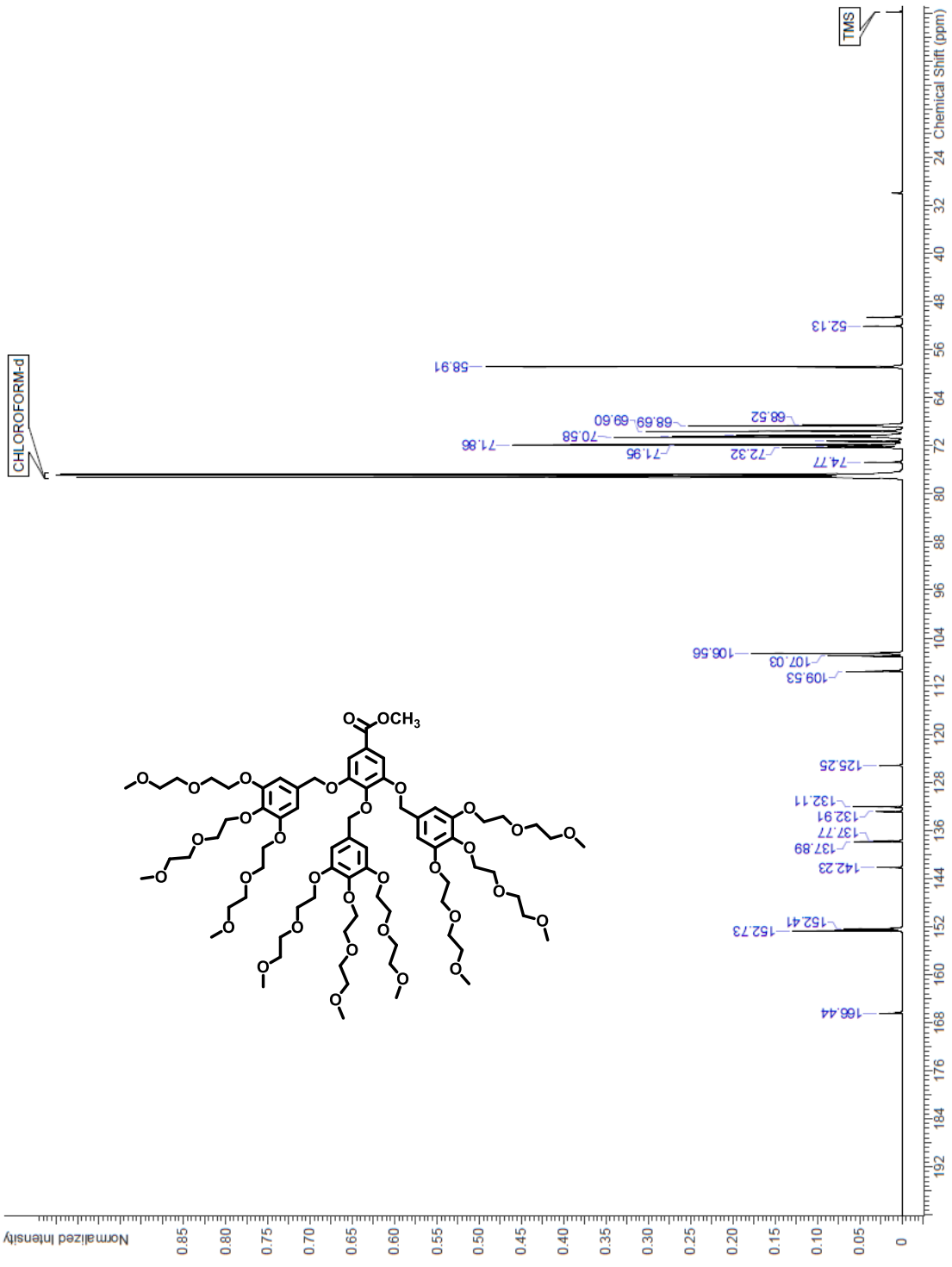

Cl
C8H17O
OC8H17
OC8H17
Chemical Shift (ppm)
Normalized Intensity
0.89
0.88
0.90
1.29
1.31
1.30
1.33
1.47
1.49
1.50
1.72
1.74
1.79
1.80
1.82
1.83
3.97
3.93
3.95
3.96
3.99
4.52
6.57
9.00
24.46
6.00
6.41
6.00
1.81
1.87

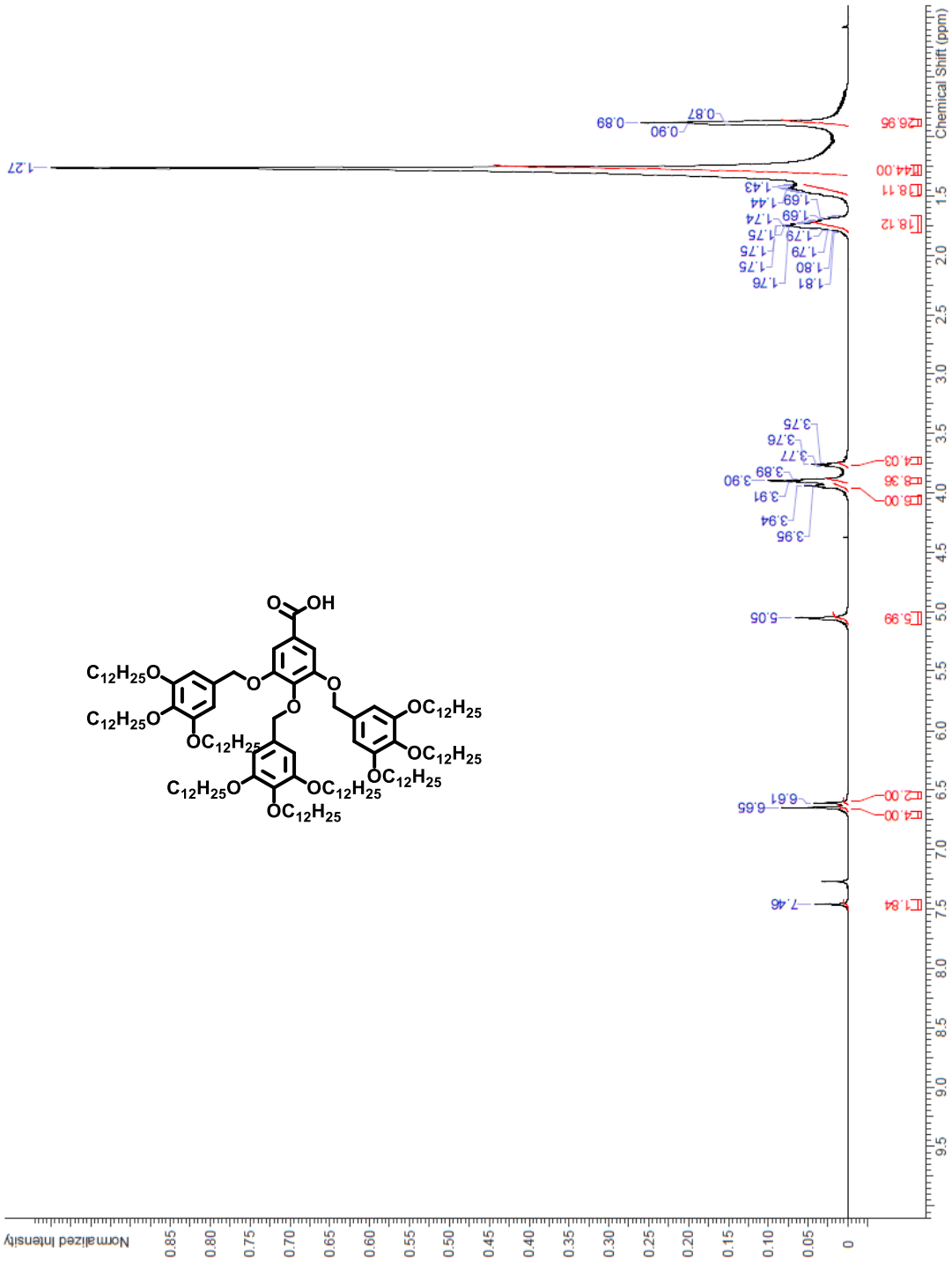

Water
CHLOROFORM-d
Cl
$C_{12}H_{25}O$
$OC_{12}H_{25}$
$OC_{12}H_{25}$
Chemical Shift (ppm)
Normalized Intensity

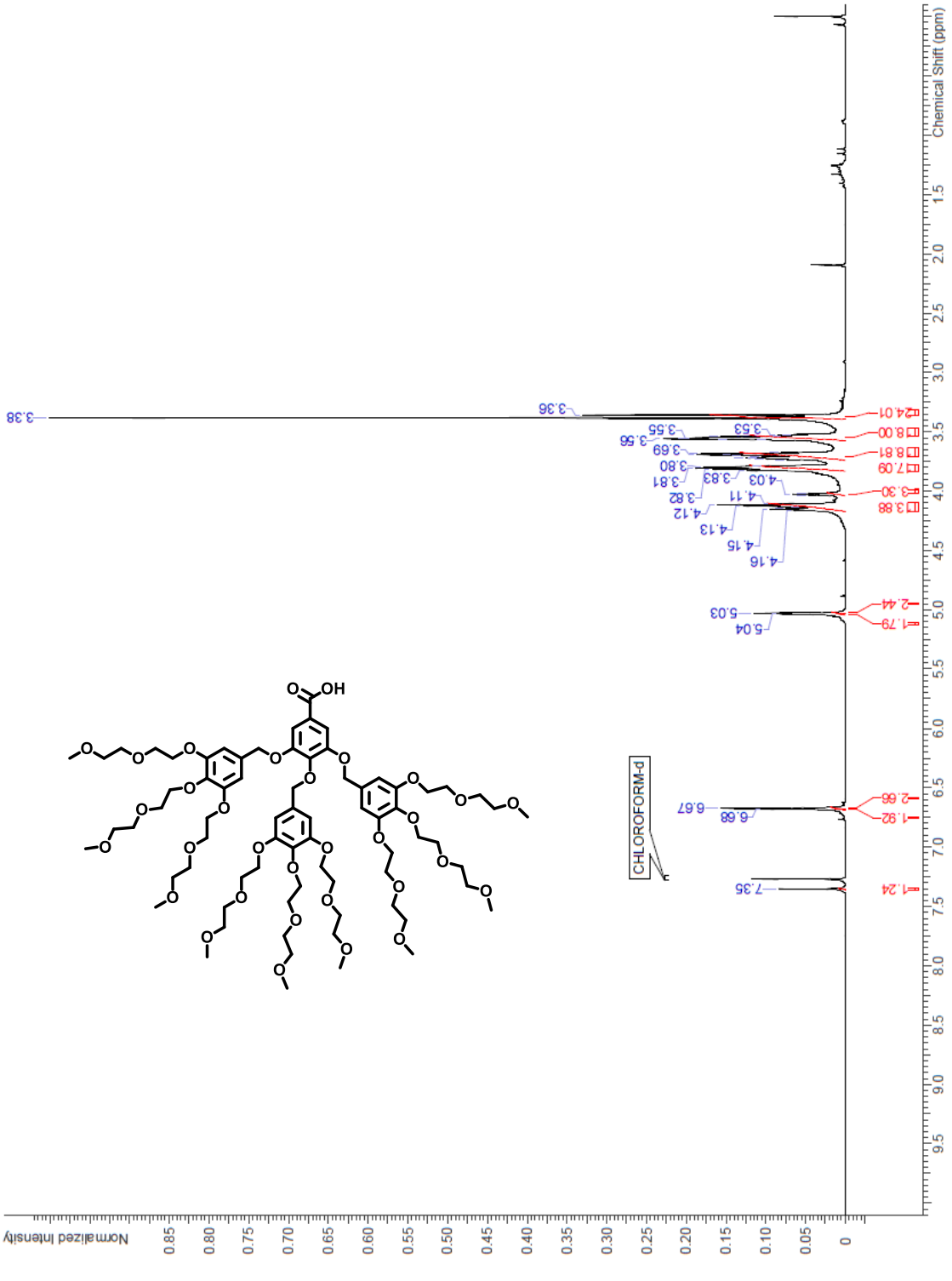

Chemical Shift (ppm)
Normalized Intensity
0.88
1.29
1.43
1.74
3.76
3.89
3.93
5.04
6.62
6.64
7.38
27.00
72.22
18.12
18.20
4.00
11.24
6.23
5.61
5.74
1.69
OCH3
C8H17O
C8H17O
OC8H17
OC8H17
OC8H17
C8H17O
OC8H17
OC8H17

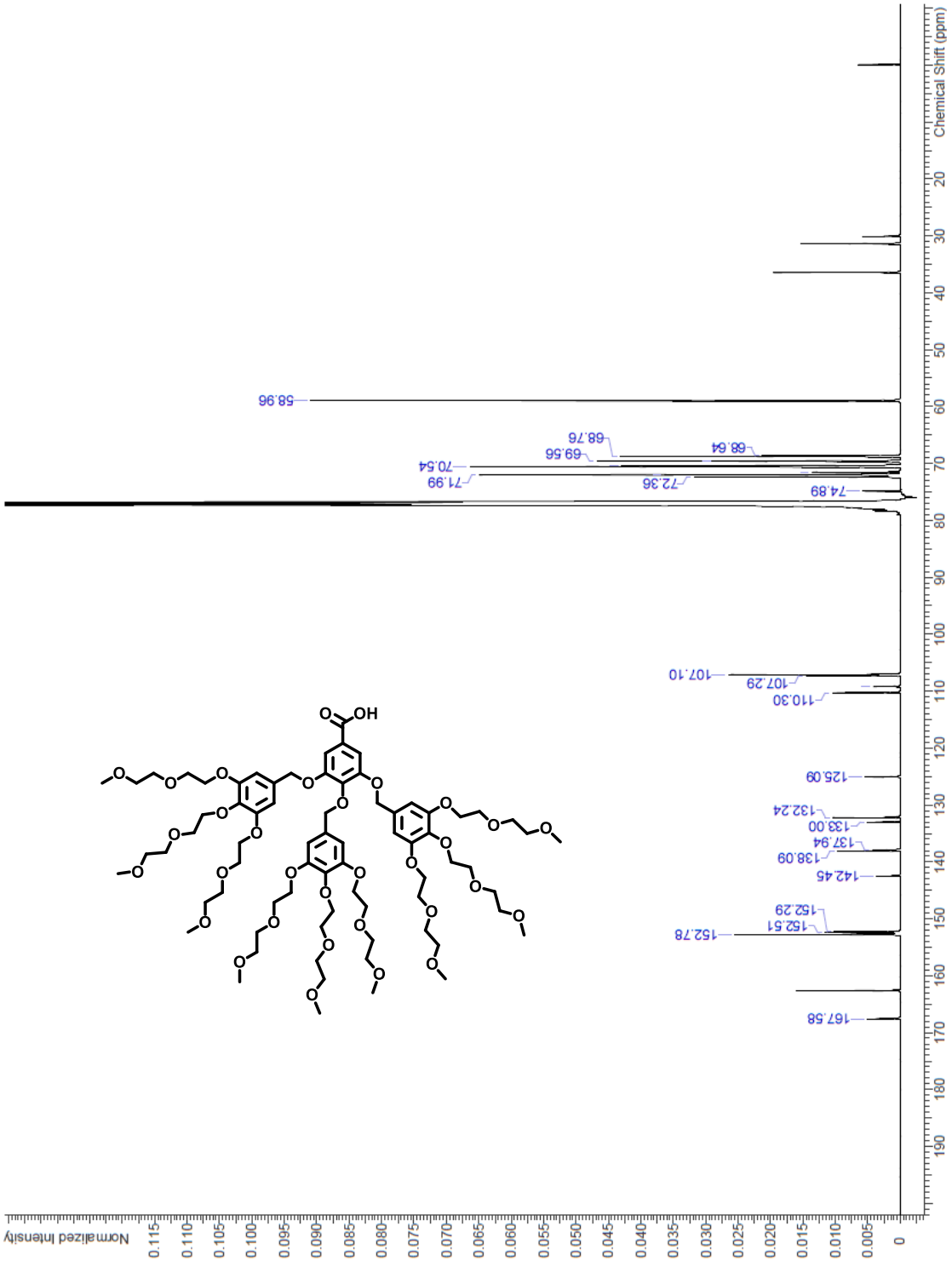

Chemical Shift (ppm)
Normalized Intensity
0.87
0.89
1.27
1.74
1.75
1.75
3.75
3.76
3.77
3.89
3.94
3.95
5.04
5.96
6.59
6.62
6.64
27.22
45.24
8.46
8.33
3.54
1.30
5.00
1.88
4.06
1.66
OCH3
C12H25O
C12H25O
OC12H25
C12H25O
OC12H25
OC12H25
OC12H25
OC12H25
OC12H25

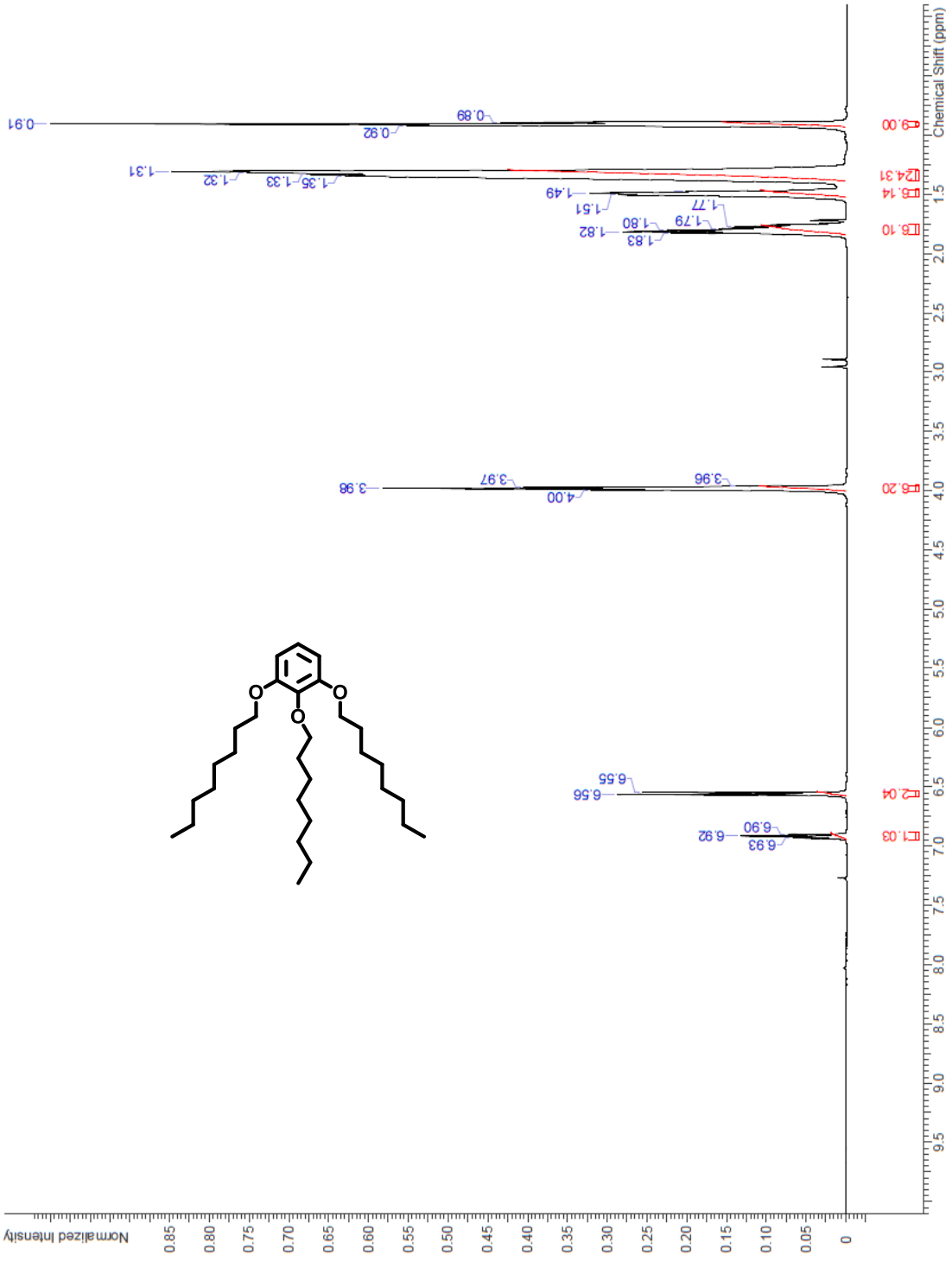

Chemical Shift (ppm)
Normalized Intensity
OCH3
3.35
3.37
3.34
3.63
3.64
3.54
3.56
3.55
3.60
3.81
3.86
3.96
4.08
4.09
4.10
4.15
4.16
5.02
6.63
6.65
7.27
7.32
2.00
2.63
5.65
7.89
7.03
5.73
5.35
5.96
4.18
4.02
2.86
6.96

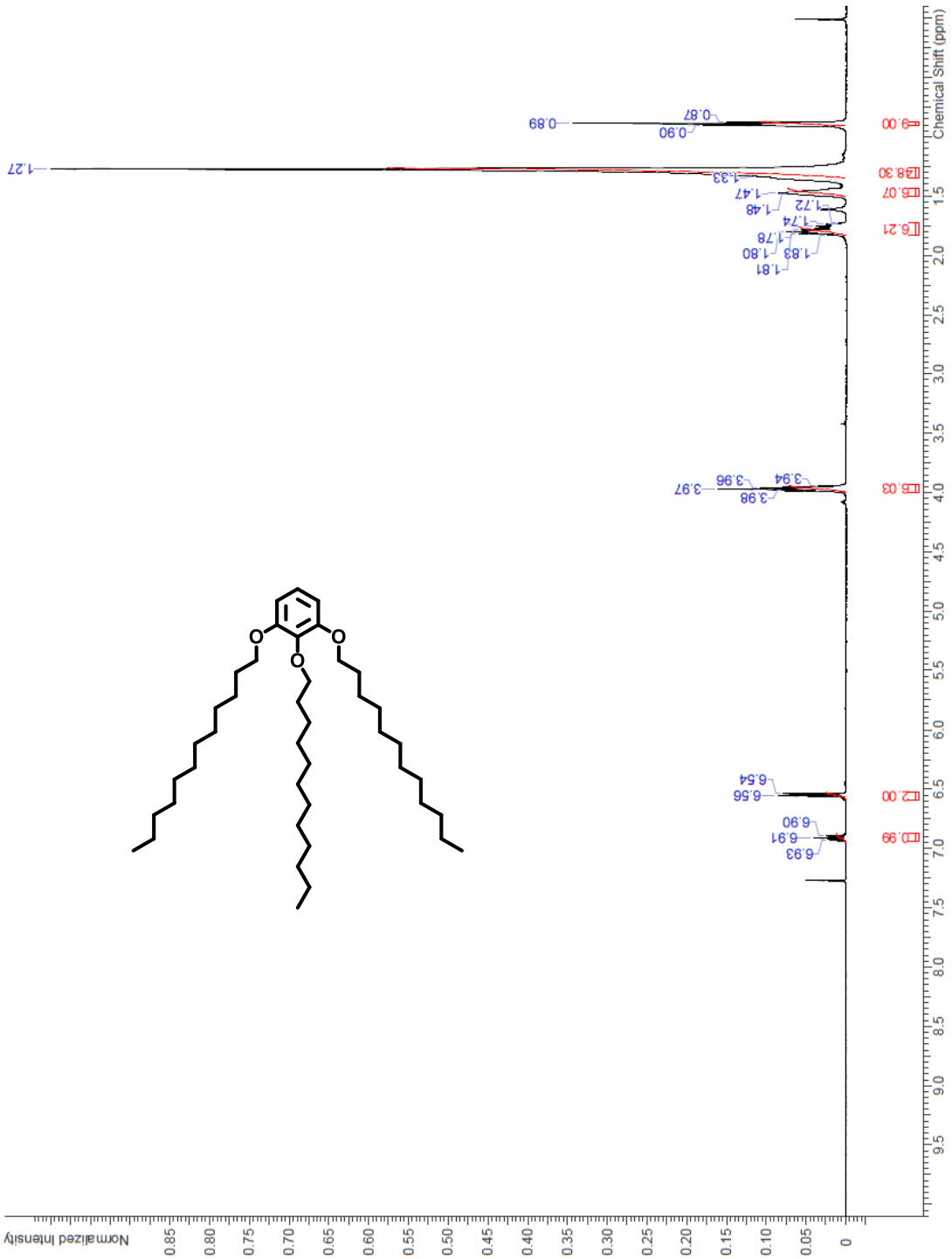

TMS
CHLOROFORM-d
52.13
58.91
68.52
68.59
69.60
70.58
71.86
71.96
72.32
74.77
106.56
107.03
109.53
125.25
132.11
132.91
137.77
137.89
142.23
152.41
152.73
166.44
OCH3
Chemical Shift (ppm)
Normalized Intensity

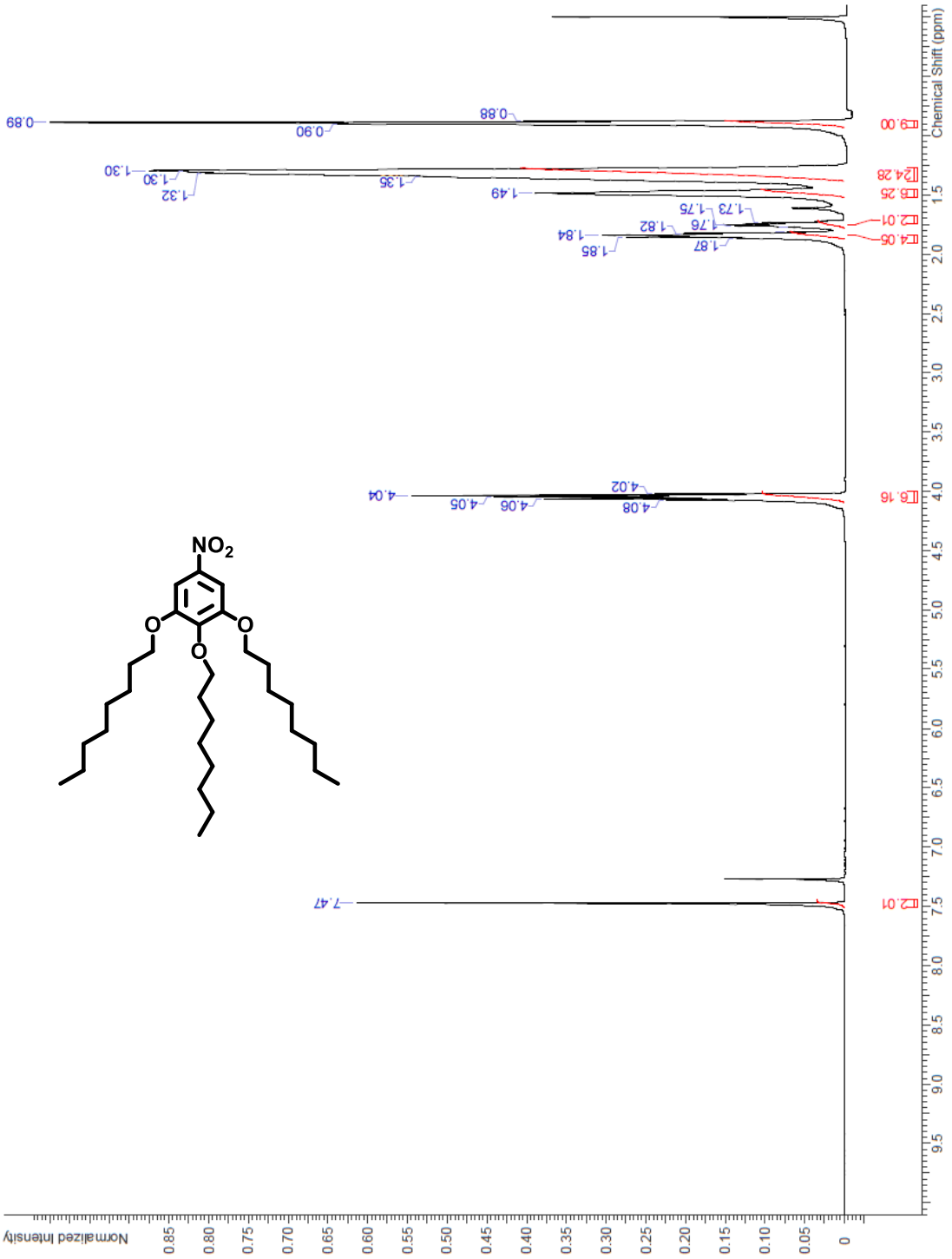

Chemical Shift (ppm)
Normalized Intensity
OH
O
C12H25O
OC12H25

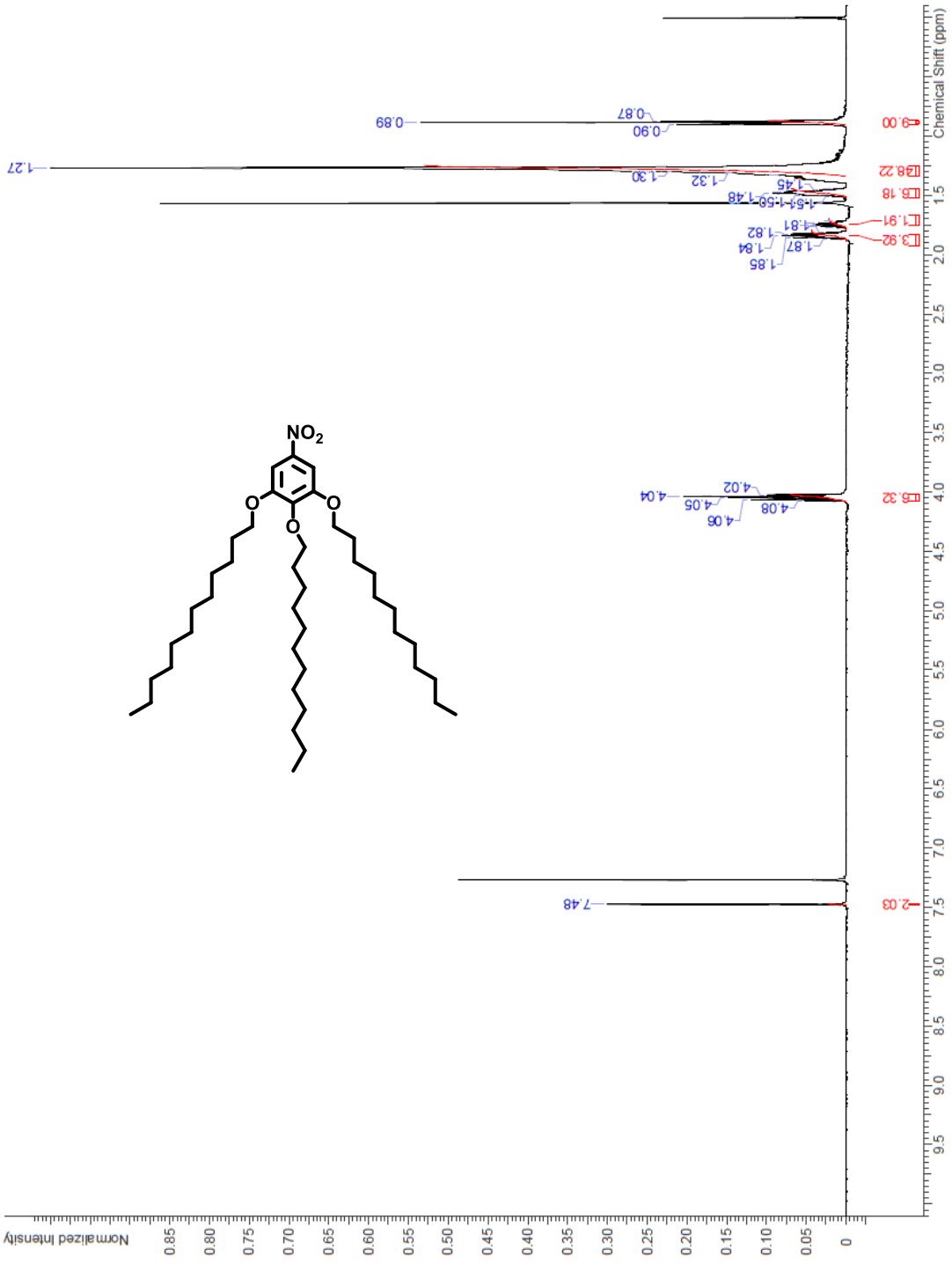

Chemical Shift (ppm)
Normalized Intensity
CHLOROFORM-d
OH
O
7.35
6.68
6.67
5.04
5.03
4.16
4.15
4.13
4.12
4.11
4.03
3.83
3.82
3.81
3.80
3.69
3.56
3.55
3.53
3.38
3.36
1.24
1.92
2.66
1.79
2.44
3.30
3.88
7.09
8.81
8.00
24.01

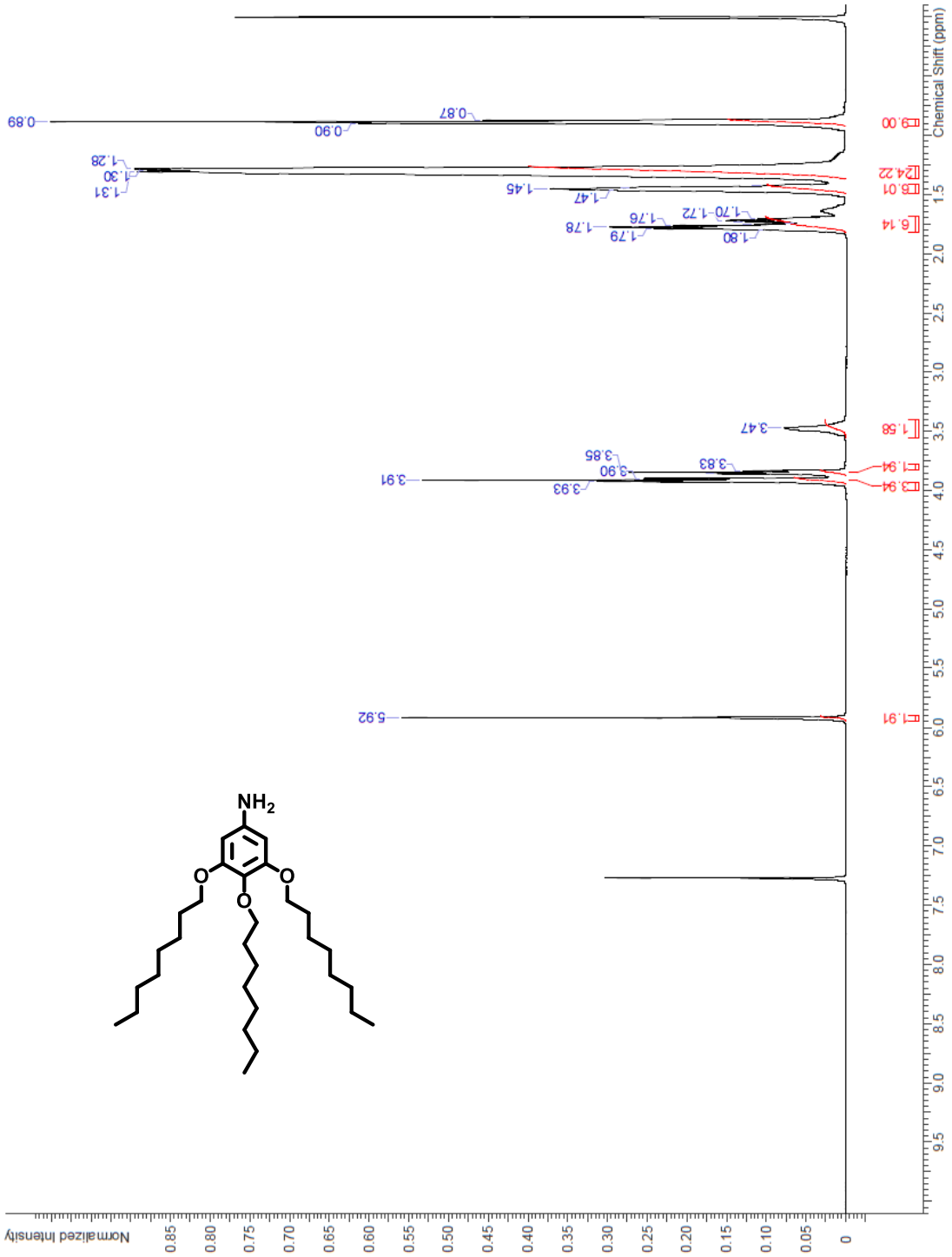

Chemical Shift (ppm)
Normalized Intensity
58.96
68.76
69.56
68.64
70.54
71.99
72.36
74.89
107.10
107.29
110.30
125.09
132.24
133.00
137.94
138.09
142.45
152.29
152.51
152.78
167.58
OH

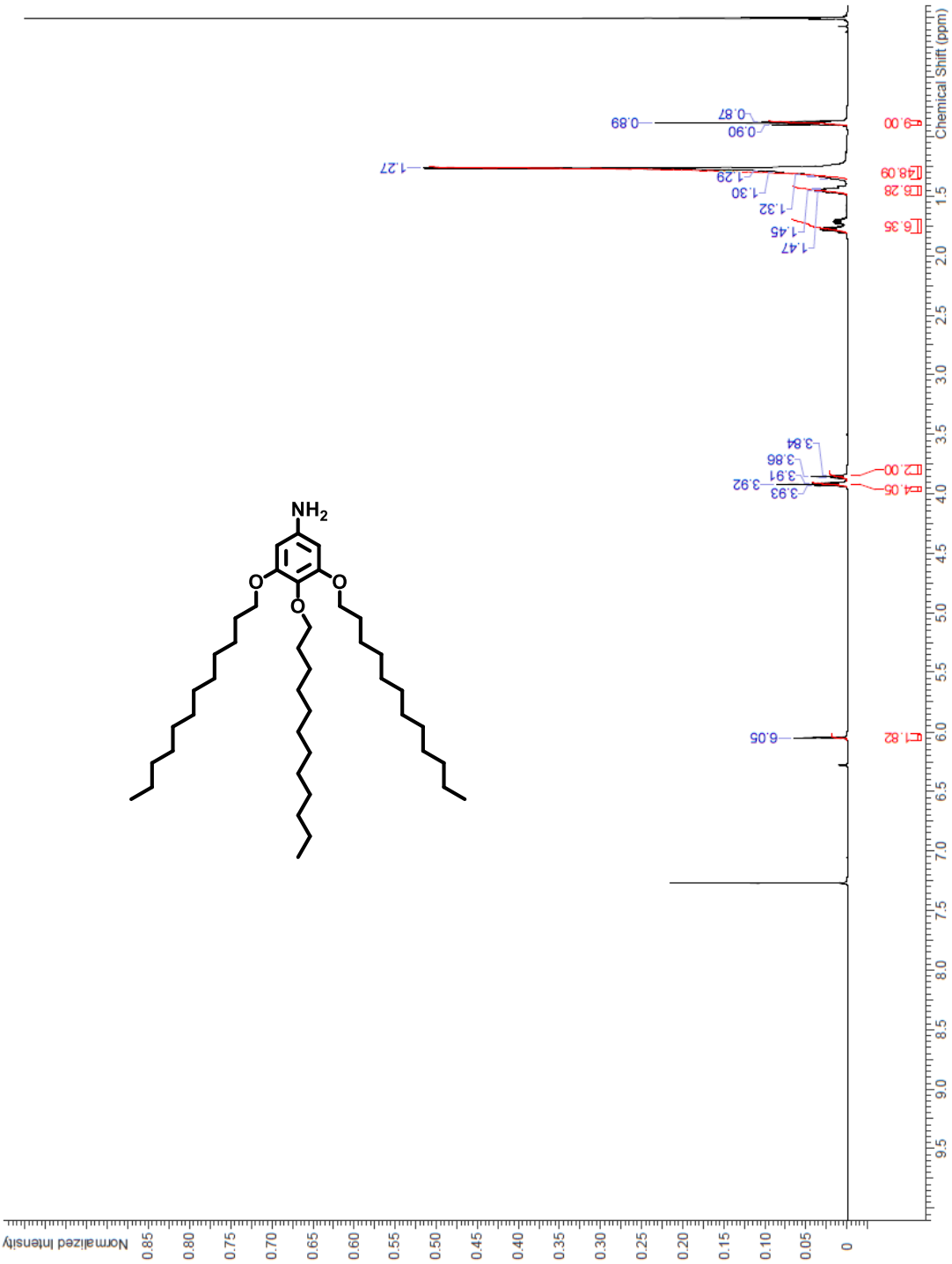

0.91
0.92
0.89
1.31
1.32
1.33
1.35
1.49
1.51
1.77
1.79
1.80
1.82
1.83
3.98
3.97
3.96
4.00
6.55
6.56
6.92
6.90
6.93
9.00
24.31
5.14
6.10
6.20
2.04
1.03
Chemical Shift (ppm)
Normalized Intensity

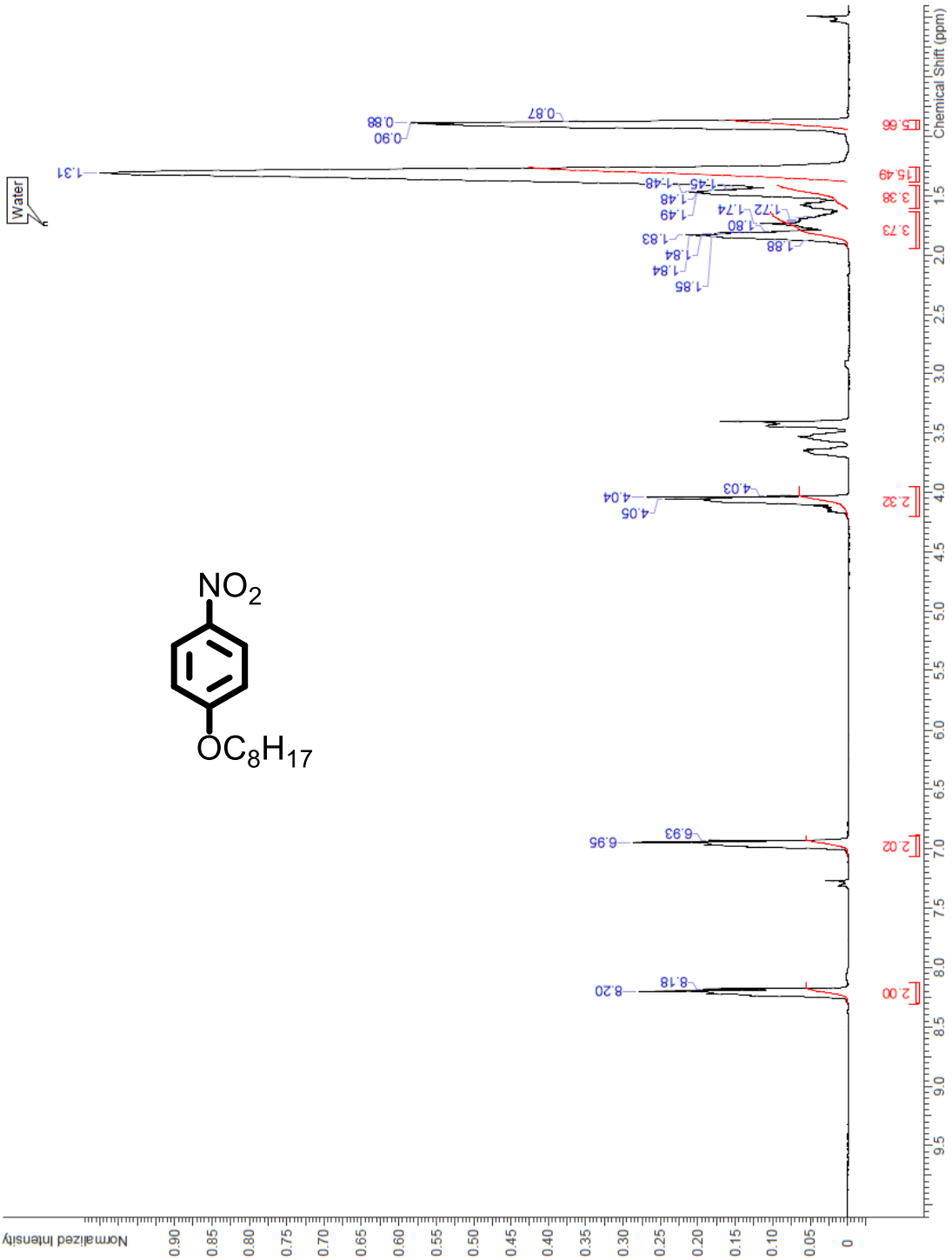

Chemical Shift (ppm)
Normalized Intensity
9.00
28.30
6.07
6.21
5.03
2.00
0.99
0.89
0.87
0.90
1.27
1.33
1.47
1.48
1.72
1.74
1.78
1.80
1.83
1.81
3.94
3.96
3.97
3.98
6.54
6.56
6.90
6.91
6.93
O
O
O

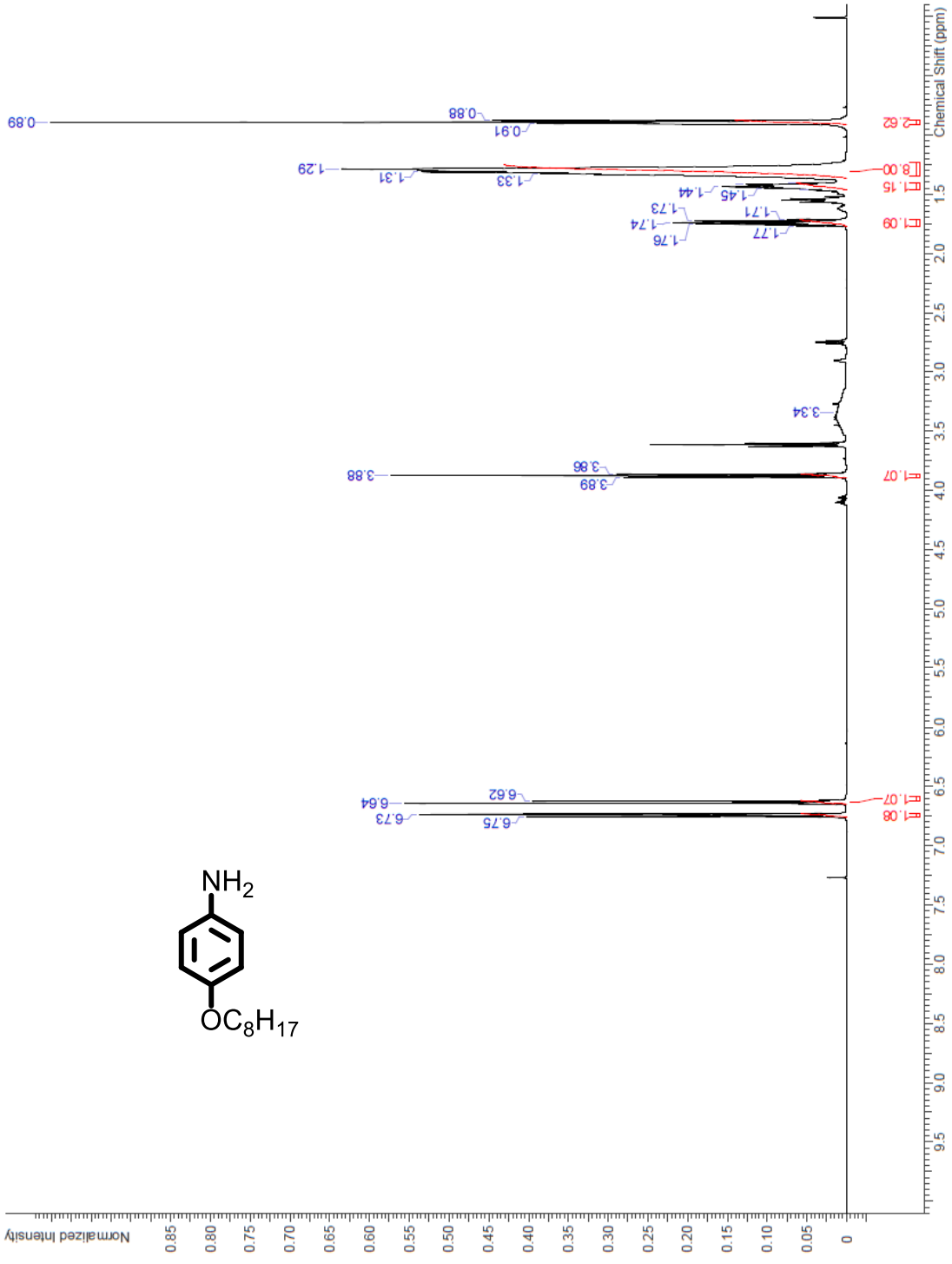

NO2
O
O
O
Chemical Shift (ppm)
Normalized Intensity
0.89
0.90
0.88
1.30
1.32
1.35
1.49
1.73
1.75
1.76
1.82
1.84
1.85
1.87
4.02
4.04
4.05
4.06
4.08
7.47
9.00
24.28
55.25
2.01
24.05
6.16
2.01

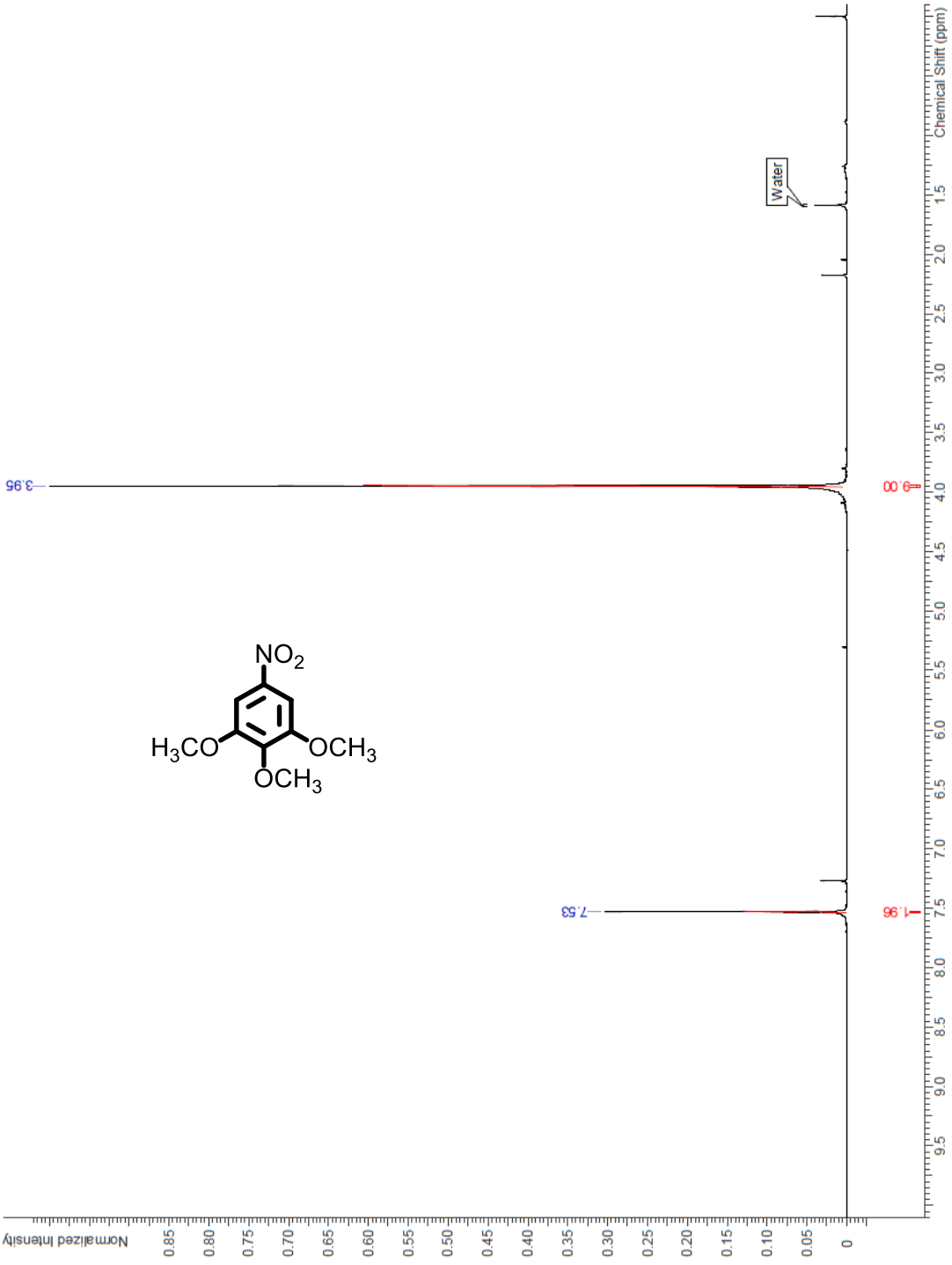

NO2
O
O
O
Chemical Shift (ppm)
Normalized Intensity
9.00
28.22
5.18
1.91
3.92
5.32
2.03
0.89
0.87
0.90
1.27
1.30
1.32
1.45
1.48
1.50
1.54
1.81
1.82
1.84
1.87
1.85
4.02
4.04
4.05
4.06
4.08
7.48

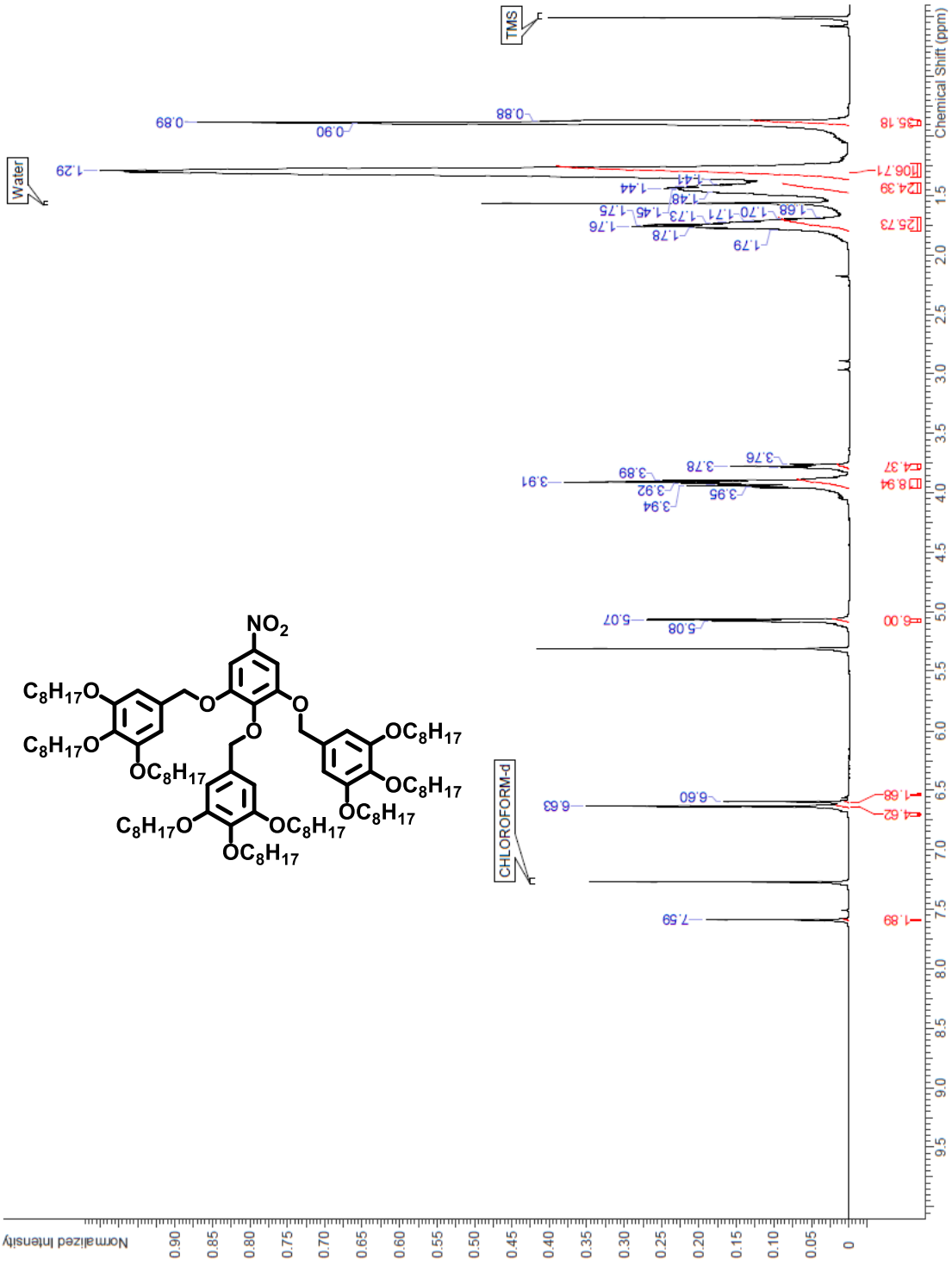

Chemical Shift (ppm)
Normalized Intensity
NH2
O
O
O
0.89
0.90
0.87
1.28
1.30
1.31
1.45
1.47
1.70-1.72
1.76
1.78
1.79
1.80
3.47
3.83
3.85
3.90
3.91
3.93
5.92
9.00
24.22
18.01
6.14
1.58
1.94
3.94
1.91

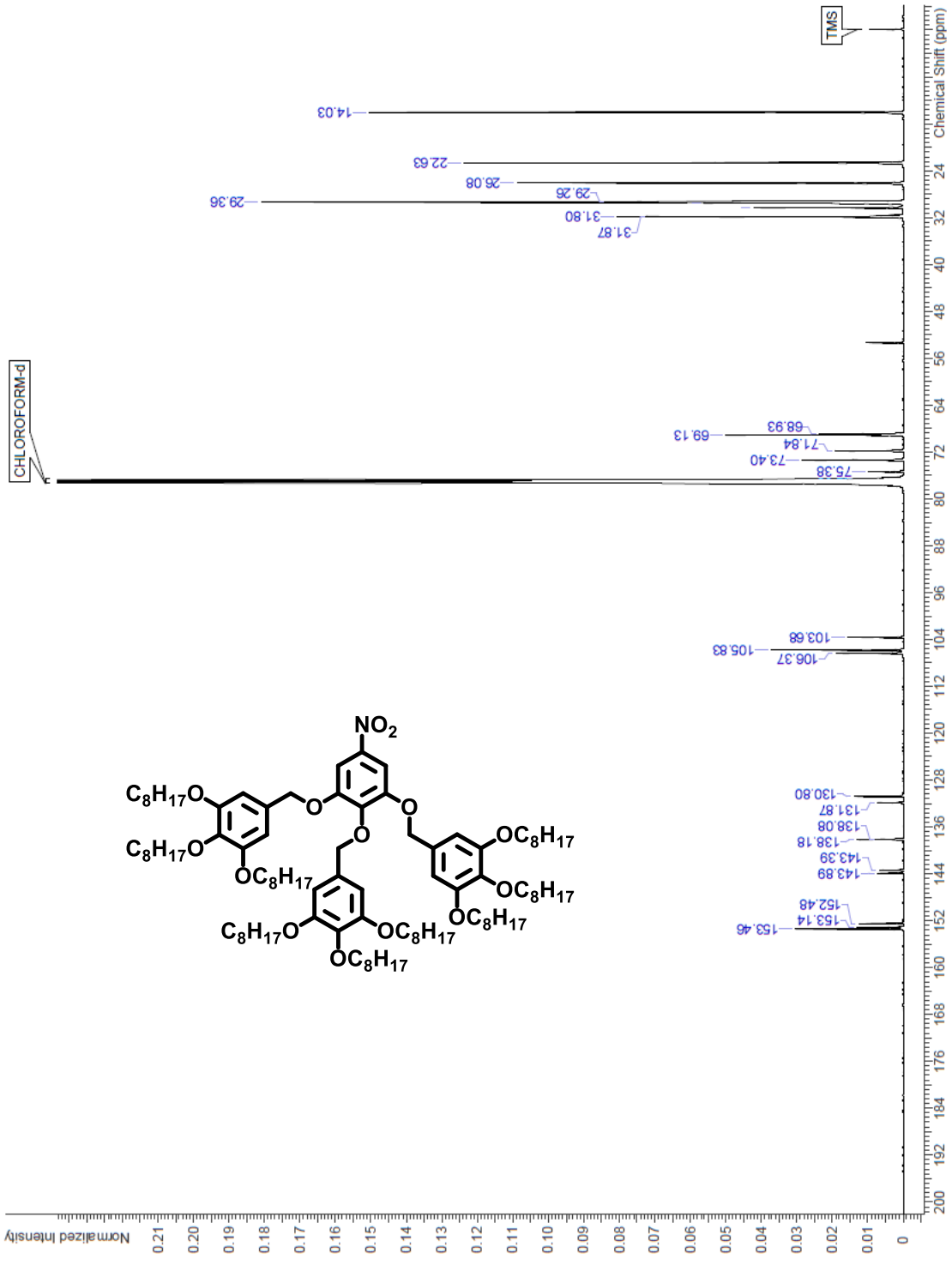

NH2
O
O
O
Chemical Shift (ppm)
Normalized Intensity
9.00
28.09
6.28
6.35
2.00
4.06
1.82
0.89
0.90
0.87
1.27
1.29
1.30
1.32
1.45
1.47
3.84
3.86
3.91
3.92
3.93
6.05

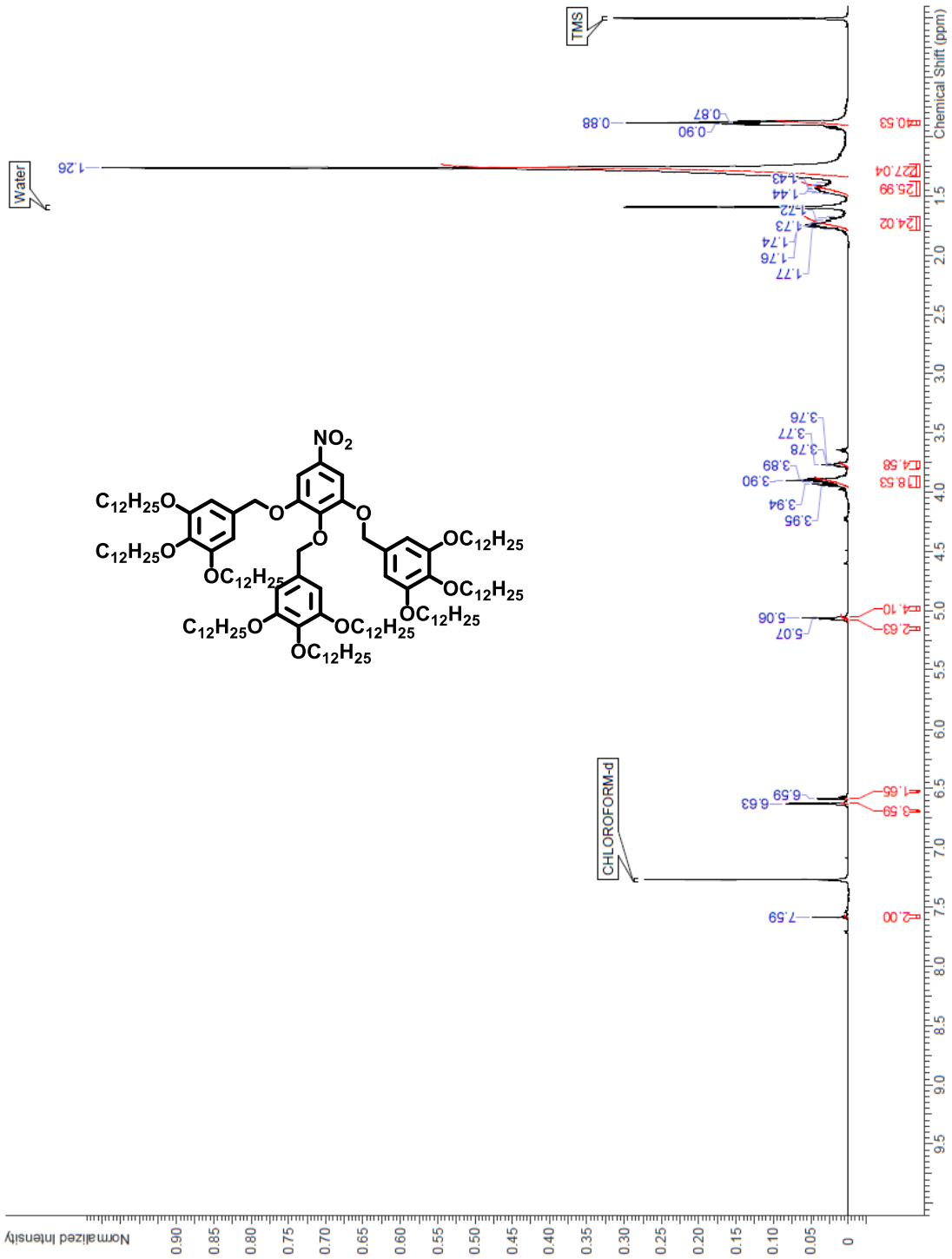

Water
0.87
0.88
0.90
1.31
1.45
1.48
1.48
1.49
1.72
1.74
1.80
1.83
1.84
1.84
1.85
1.88
4.03
4.04
4.05
6.93
6.95
8.18
8.20
5.66
5.49
3.38
3.73
2.32
2.02
2.00
NO2
OC8H17
Chemical Shift (ppm)
Normalized Intensity

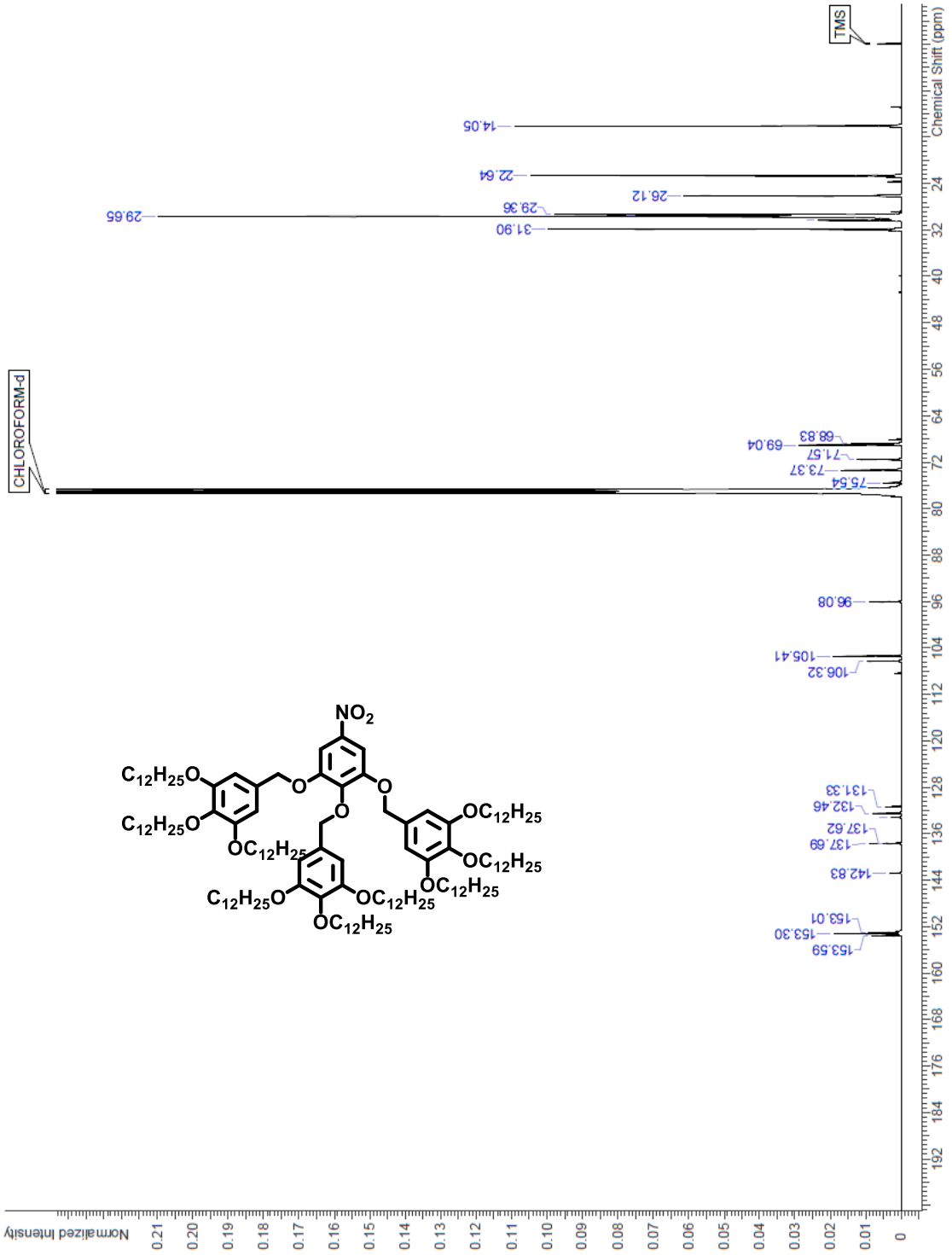

Chemical Shift (ppm)
Normalized Intensity
0.89
0.88
0.91
1.29
1.31
1.33
1.44
1.45
1.71
1.73
1.74
1.76
1.77
3.34
3.88
3.86
3.89
6.62
6.64
6.73
6.75
2.62
8.00
1.15
1.09
1.07
1.08
NH2
OC8H17

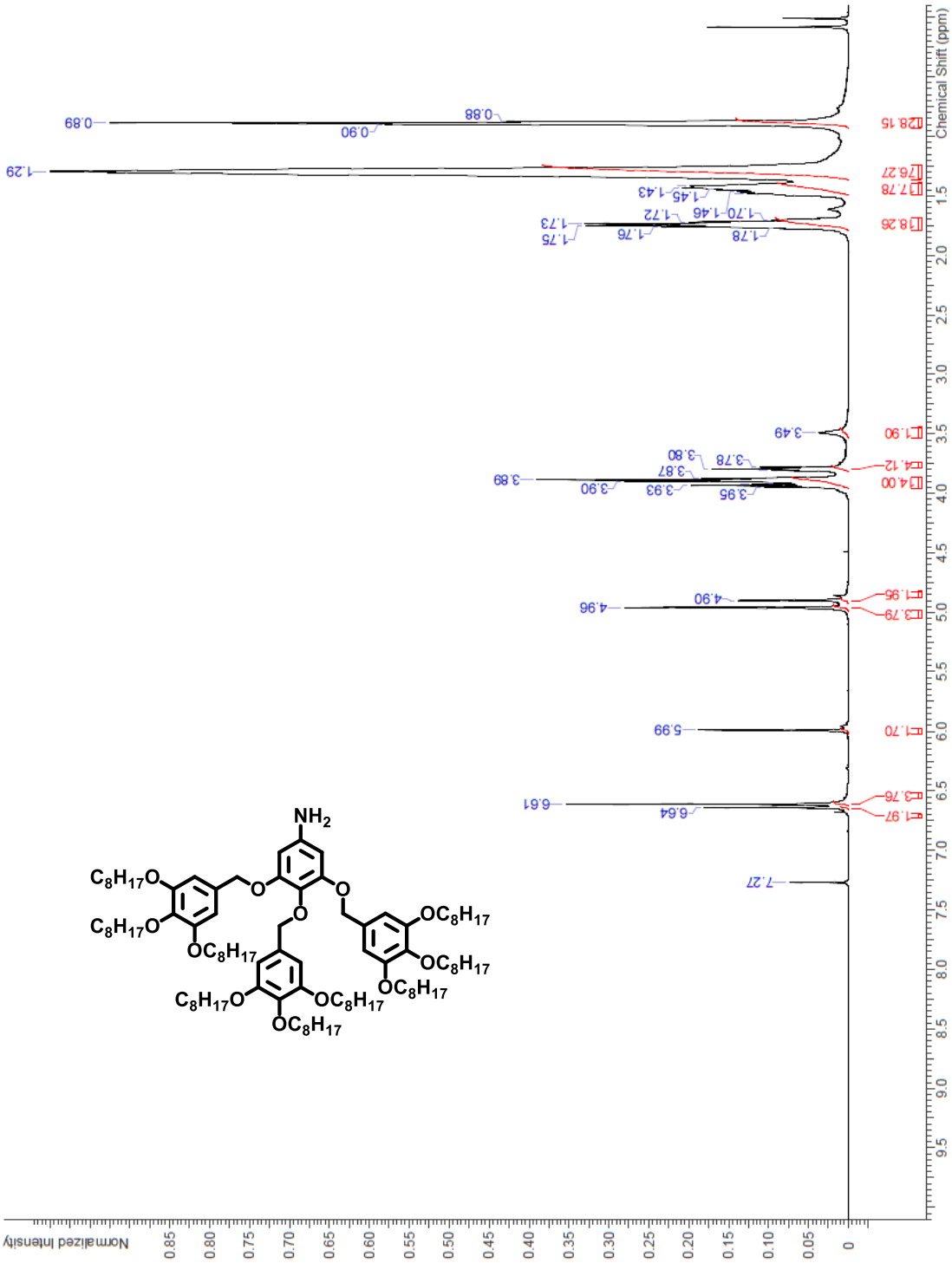

Water
3.95
9.00
7.53
1.96
Chemical Shift (ppm)
Normalized Intensity
NO2
H3CO
OCH3
OCH3

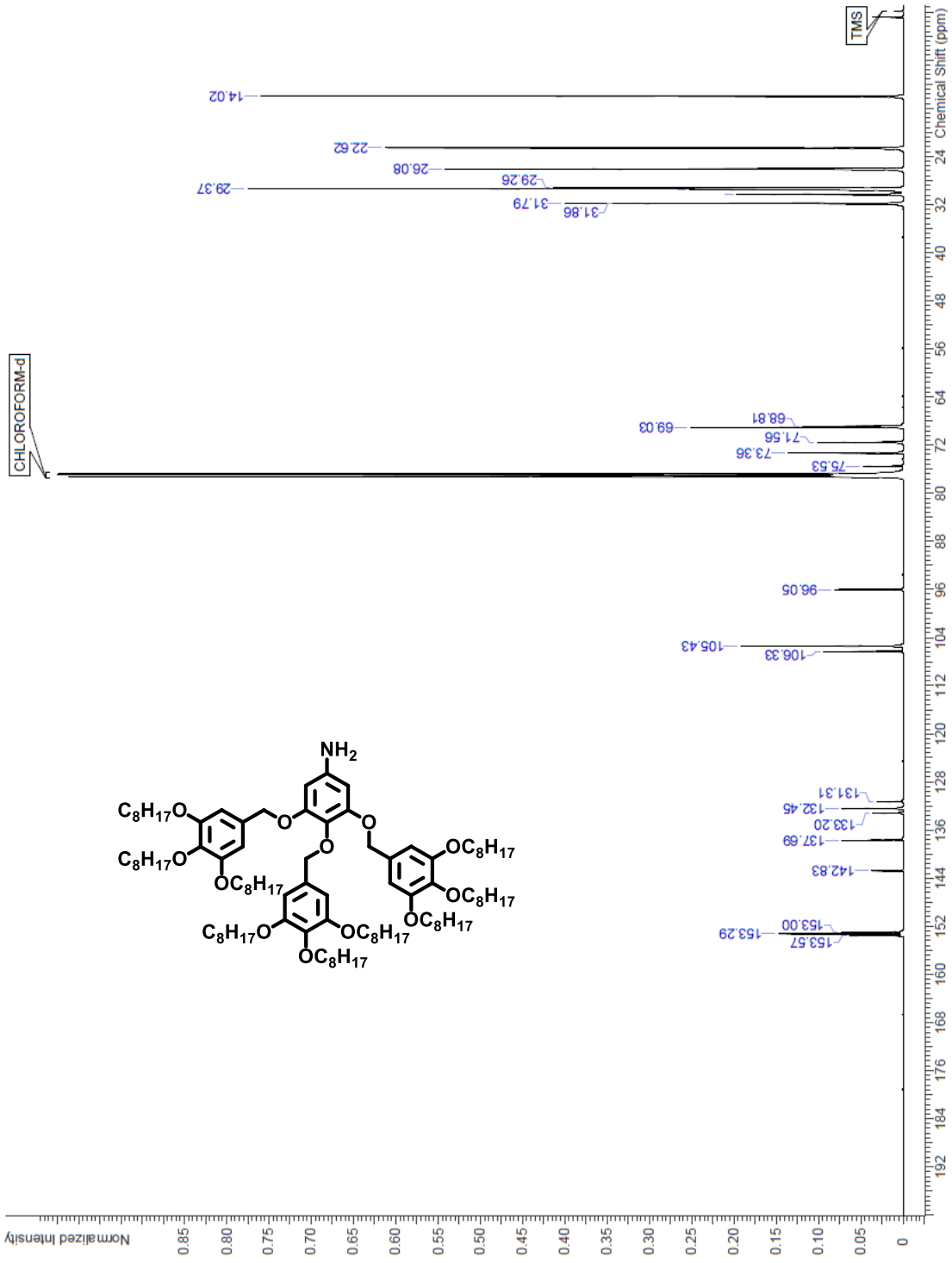

TMS
Water
CHLOROFORM-d
0.89
0.90
0.88
1.29
1.41
1.44
1.48
1.68
1.70
1.71
1.73
1.75
1.76
1.78
1.79
3.76
3.78
3.89
3.91
3.92
3.94
3.95
5.07
5.08
6.60
6.63
7.59
35.18
106.71
24.39
25.73
24.37
8.94
6.00
1.68
24.62
1.89
Chemical Shift (ppm)
Normalized Intensity
NO_2
$C_8H_{17}O$
OC_8H_{17}

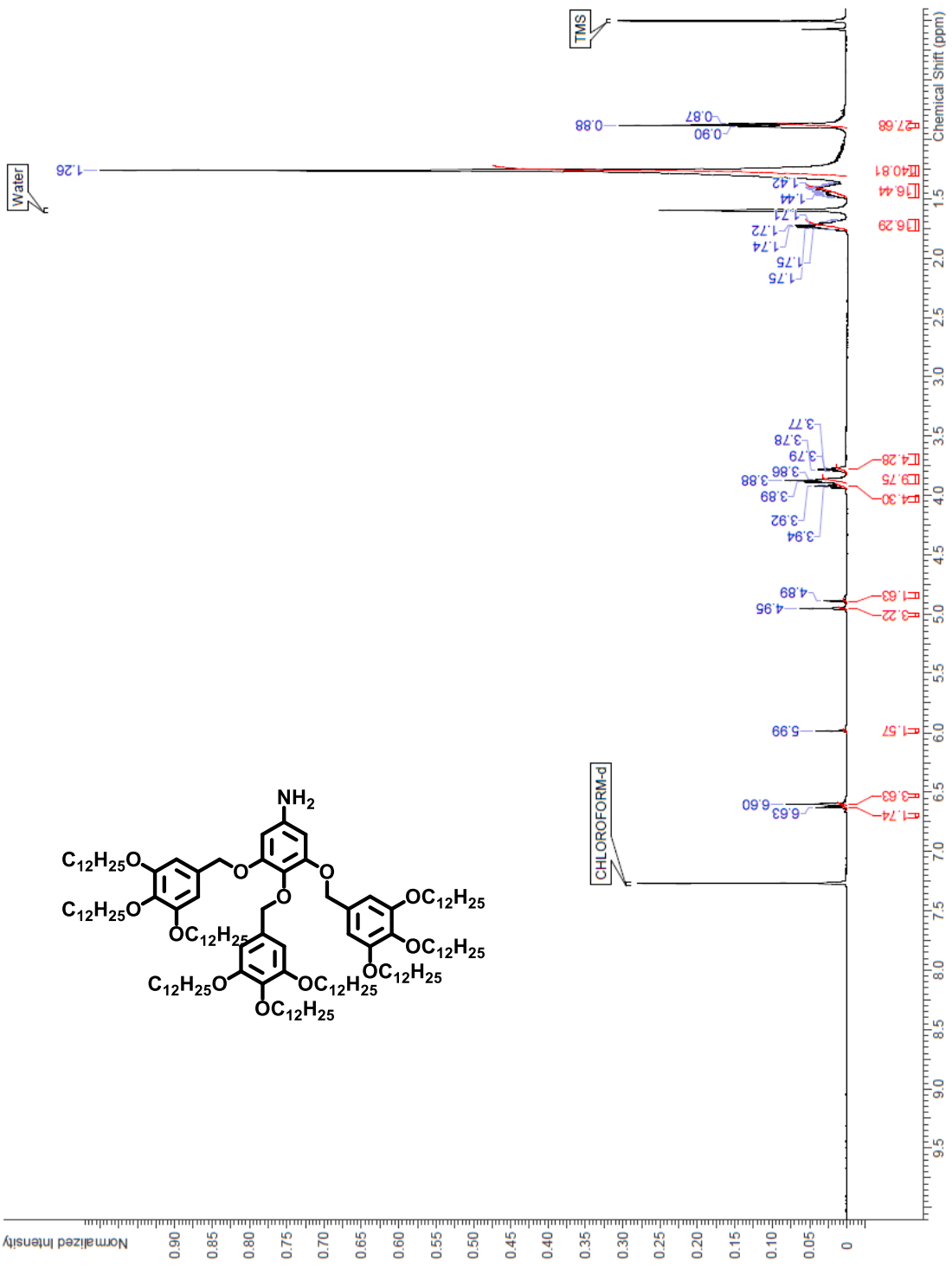

TMS
CHLOROFORM-d
14.03
22.63
26.08
29.26
29.36
31.80
31.87
68.93
69.13
71.84
73.40
75.38
103.68
105.83
106.37
130.80
131.87
138.08
138.18
143.39
143.89
152.48
153.14
153.46
NO2
C8H17O
C8H17O
OC8H17
OC8H17
OC8H17
C8H17O
OC8H17
OC8H17
Chemical Shift (ppm)
Normalized Intensity

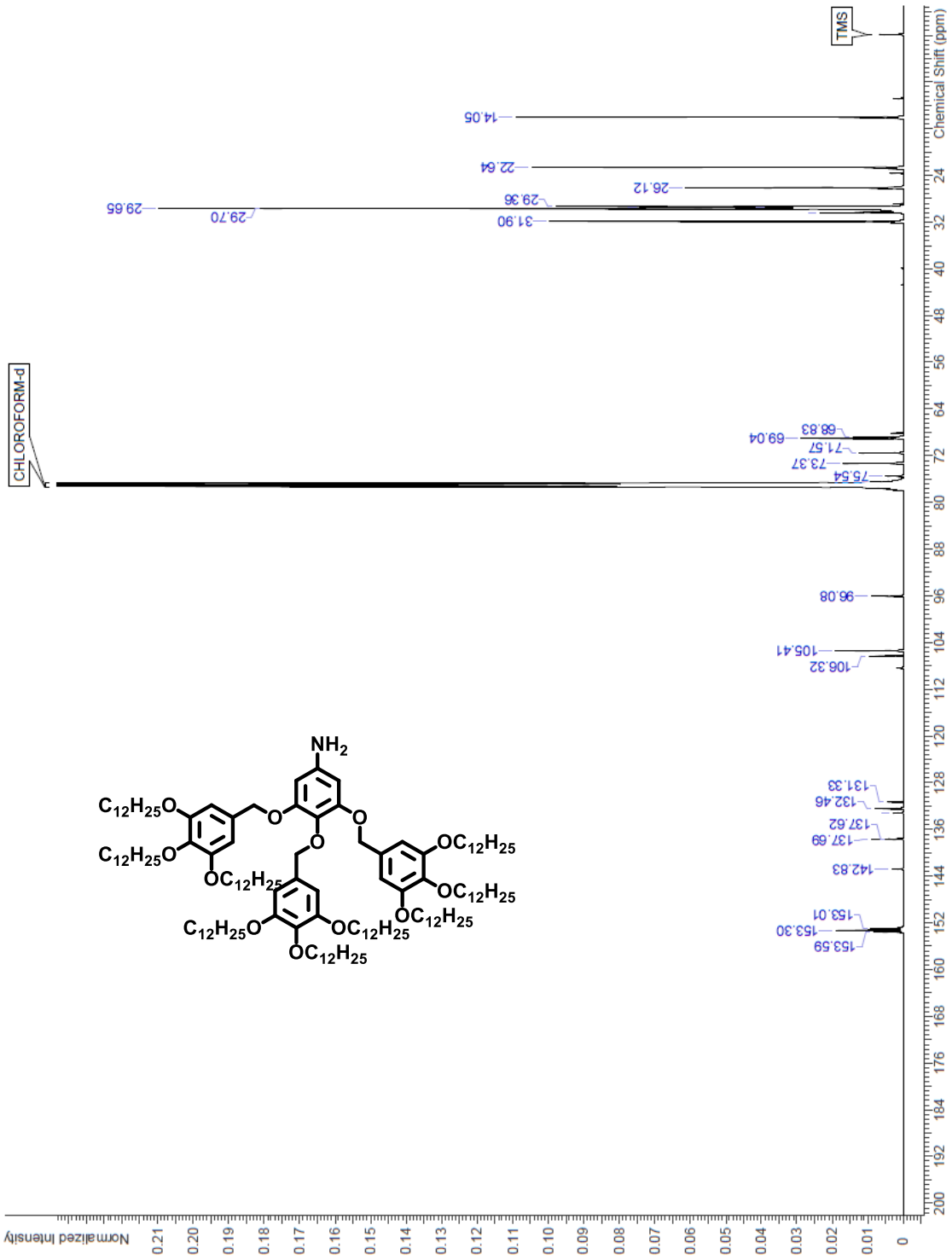

TMS
Water
CHLOROFORM-d
0.87
0.88
0.90
1.26
1.43
1.44
1.72
1.73
1.74
1.76
1.77
3.76
3.77
3.78
3.89
3.90
3.94
3.95
5.06
5.07
6.59
6.63
7.59
NO2
C12H25O
OC12H25
Chemical Shift (ppm)
Normalized Intensity

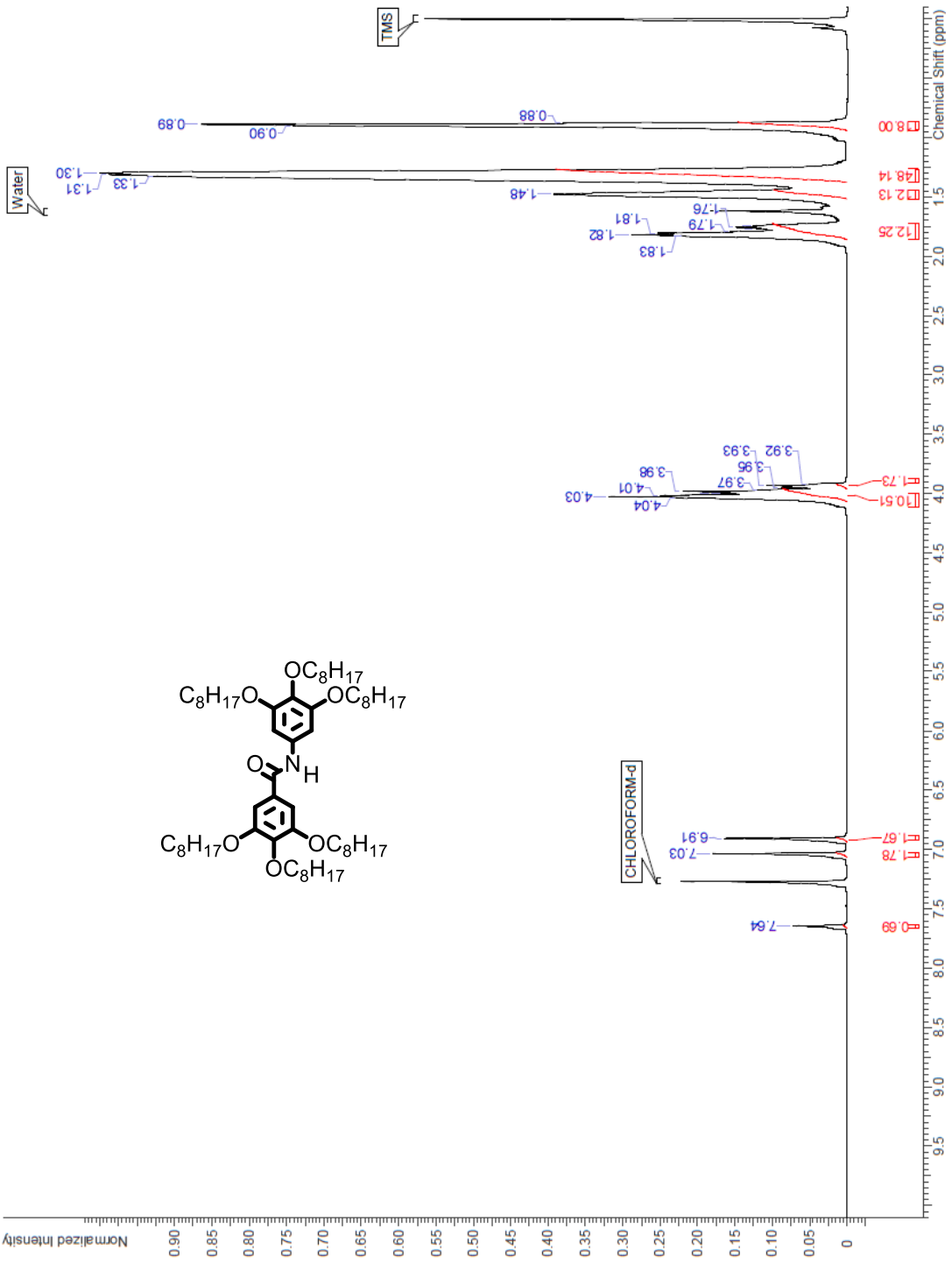

TMS
CHLOROFORM-d
14.05
22.64
26.12
29.36
29.65
31.90
68.83
69.04
71.57
73.37
75.54
96.08
105.41
106.32
131.33
132.46
137.62
137.69
142.83
153.01
153.30
153.59
NO2
C12H25O
C12H25O
OC12H25
OC12H25
OC12H25
C12H25O
OC12H25
OC12H25
Chemical Shift (ppm)
Normalized Intensity

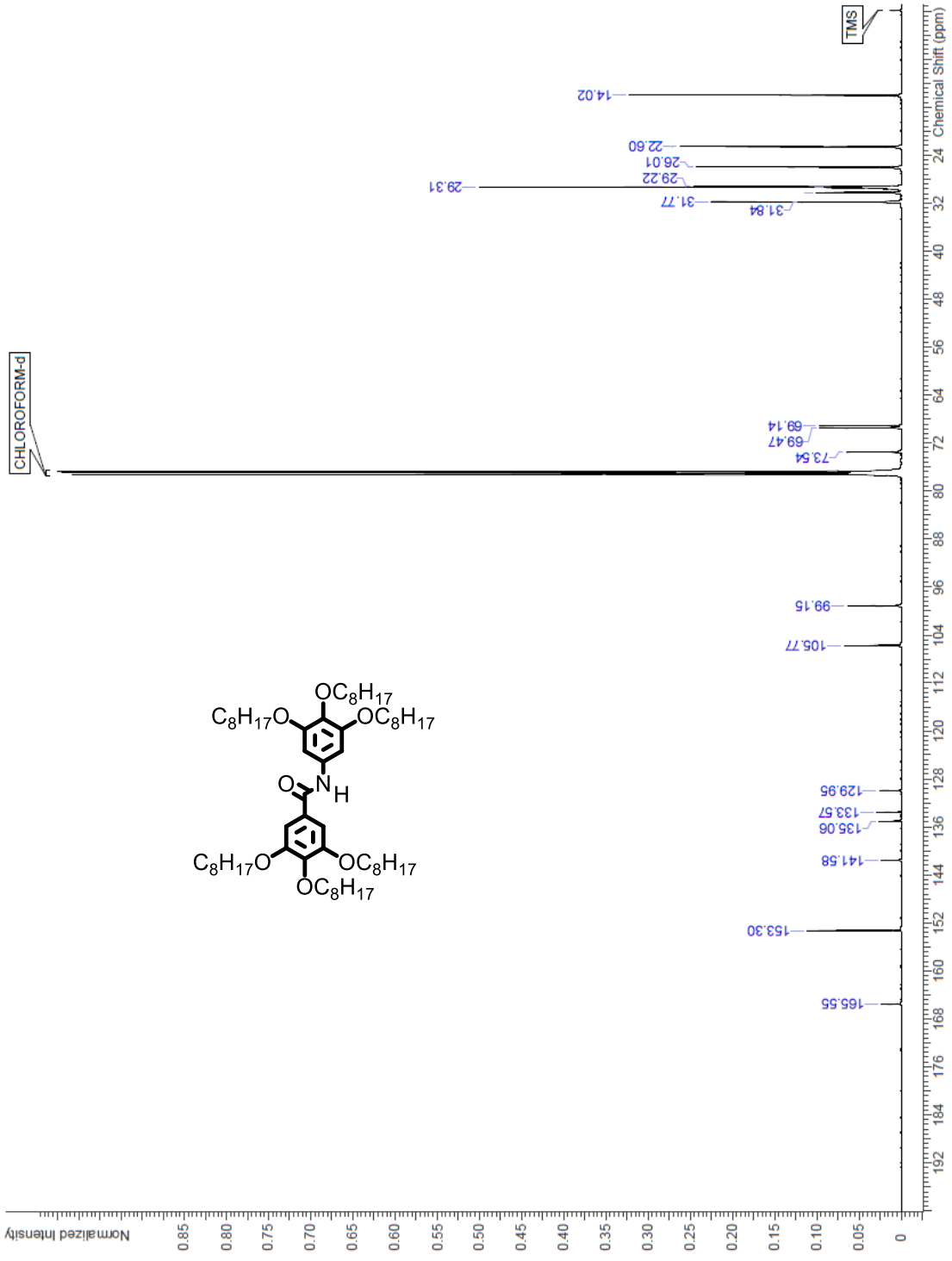

Chemical Shift (ppm)
Normalized Intensity
NH2
C8H17O
OC8H17

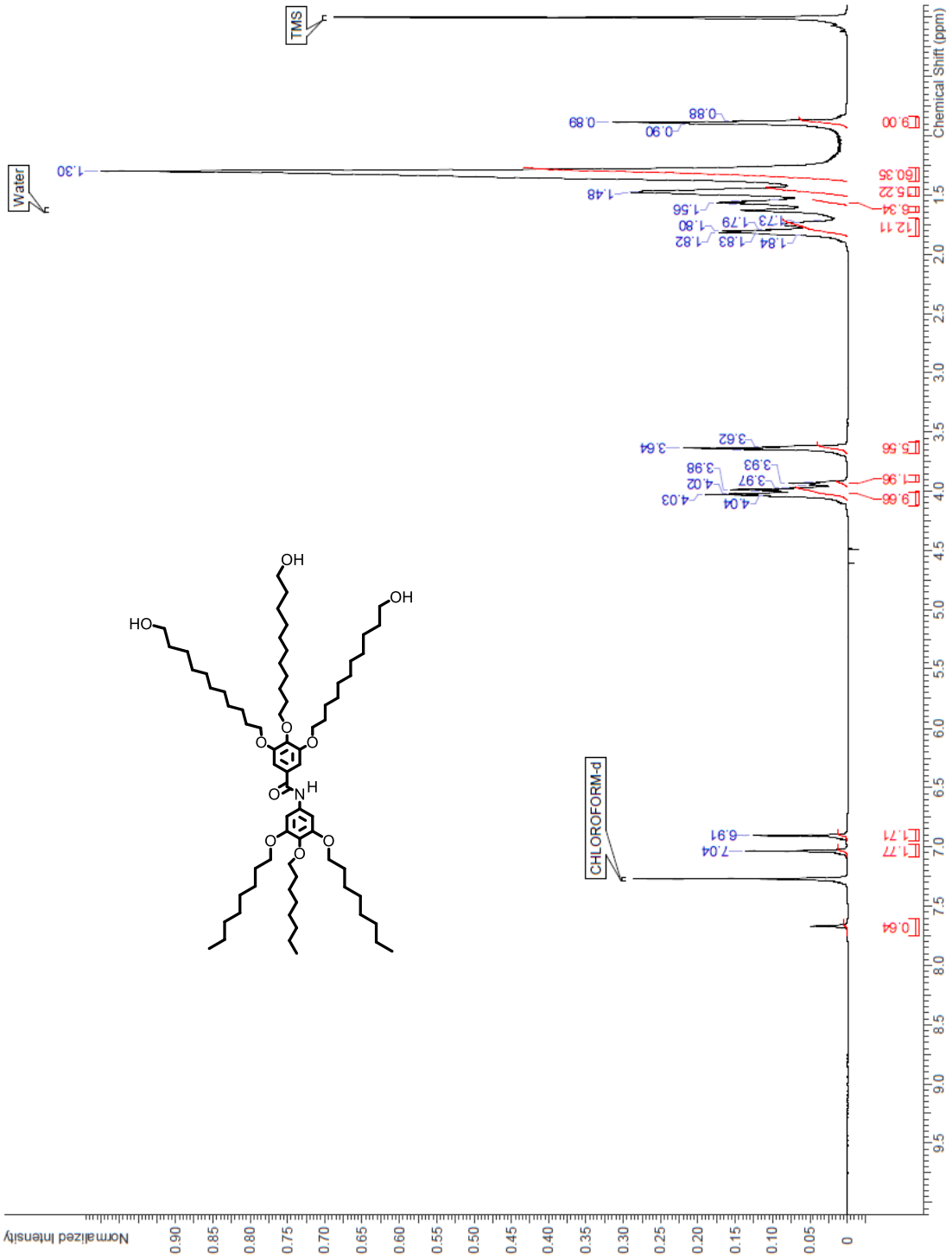

TMS
CHLOROFORM-d
14.02
22.62
26.08
29.26
29.37
31.79
31.86
68.81
69.03
71.56
73.36
75.53
96.05
106.33
105.43
131.31
132.45
133.20
137.69
142.83
153.00
153.29
153.57
NH2
C8H17O
C8H17O
OC8H17
OC8H17
OC8H17
C8H17O
OC8H17
OC8H17
Chemical Shift (ppm)
Normalized Intensity

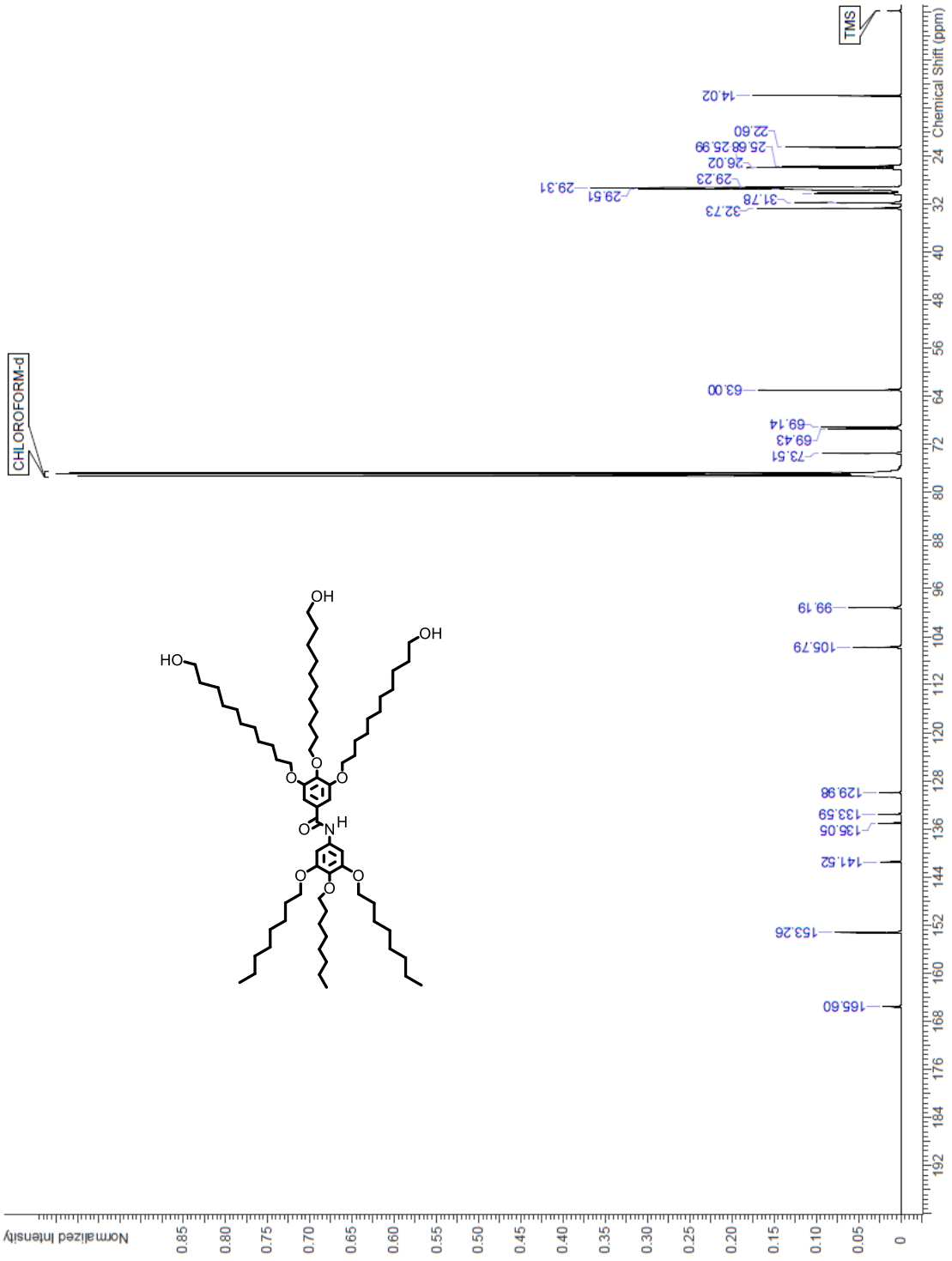

TMS
Water
CHLOROFORM-d
0.88
0.87
0.90
1.26
1.42
1.44
1.71
1.72
1.74
1.75
1.75
3.77
3.78
3.79
3.86
3.88
3.89
3.92
3.94
4.89
4.95
5.99
6.60
6.63
6.63
7.66
40.81
6.44
6.29
4.28
9.75
1.30
1.63
3.22
1.57
3.63
1.74
Chemical Shift (ppm)
Normalized Intensity
NH2
C12H25O
C12H25O
OC12H25
OC12H25
OC12H25
OC12H25
C12H25O
OC12H25
OC12H25

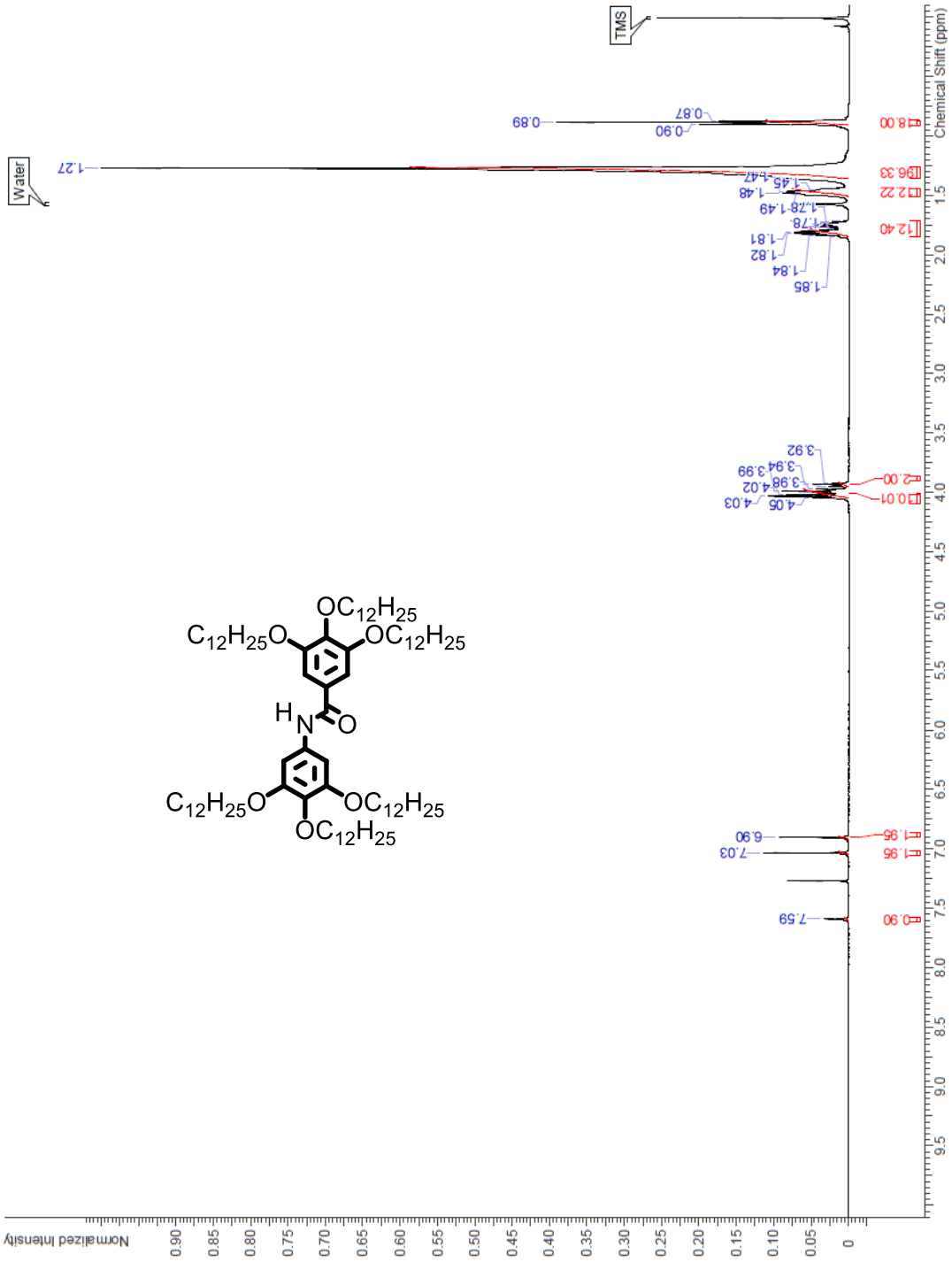

TMS
CHLOROFORM-d
14.05
22.64
26.12
29.36
29.70
29.65
31.90
68.83
69.04
71.57
73.37
75.54
96.08
105.41
106.32
131.33
132.46
137.62
137.69
142.83
153.01
153.30
153.59
NH2
C12H25O
C12H25O
OC12H25
OC12H25
OC12H25
OC12H25
OC12H25
OC12H25
Chemical Shift (ppm)
Normalized Intensity

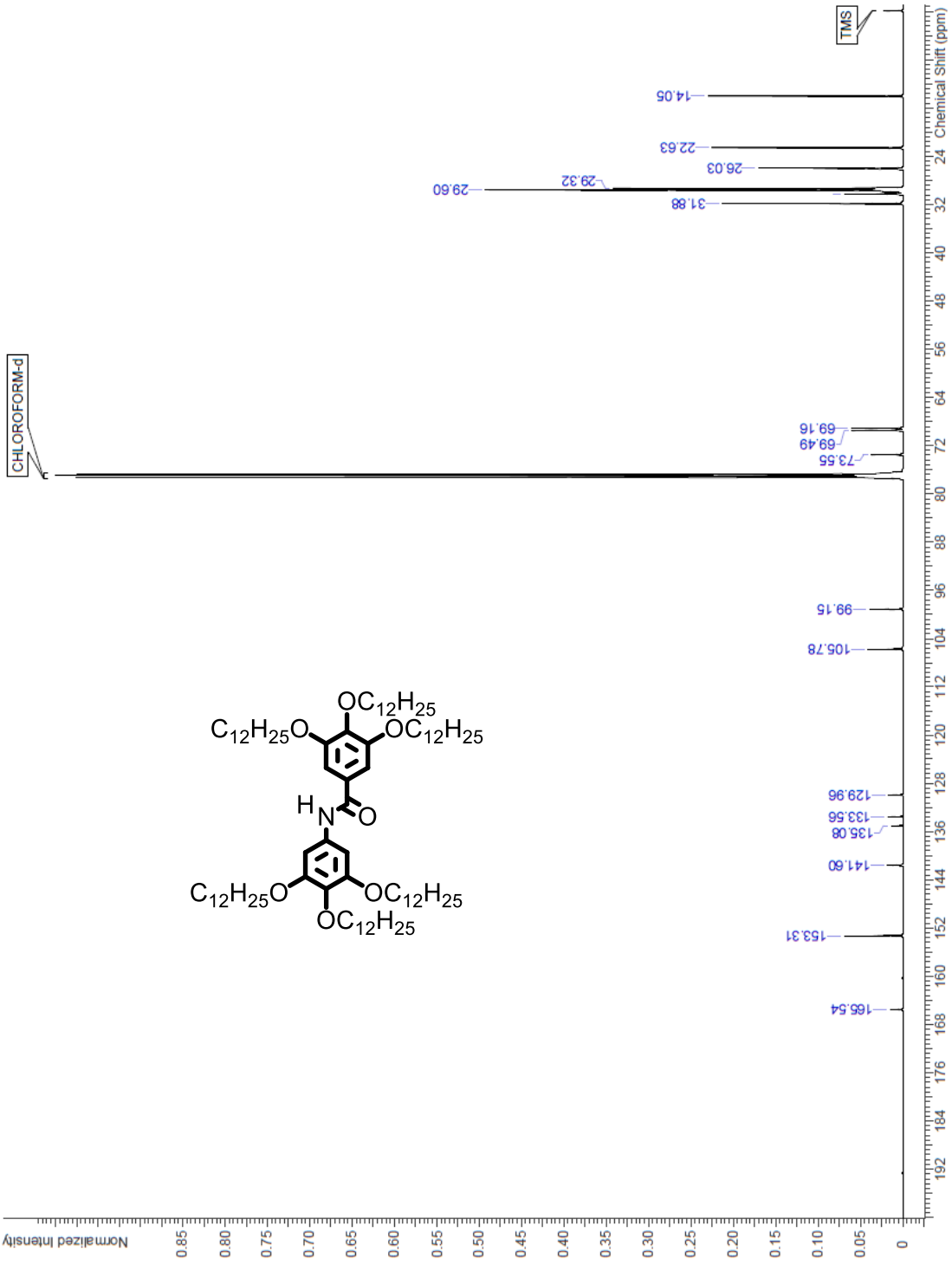

TMS
Water
CHLOROFORM-d
Chemical Shift (ppm)
Normalized Intensity
0.88
0.90
0.89
1.30
1.31
1.33
1.48
1.76
1.79
1.81
1.82
1.83
3.92
3.93
3.86
3.97
3.98
4.01
4.03
4.04
6.91
7.03
7.64
8.00
48.14
2.13
2.25
1.73
0.51
1.67
1.78
0.69

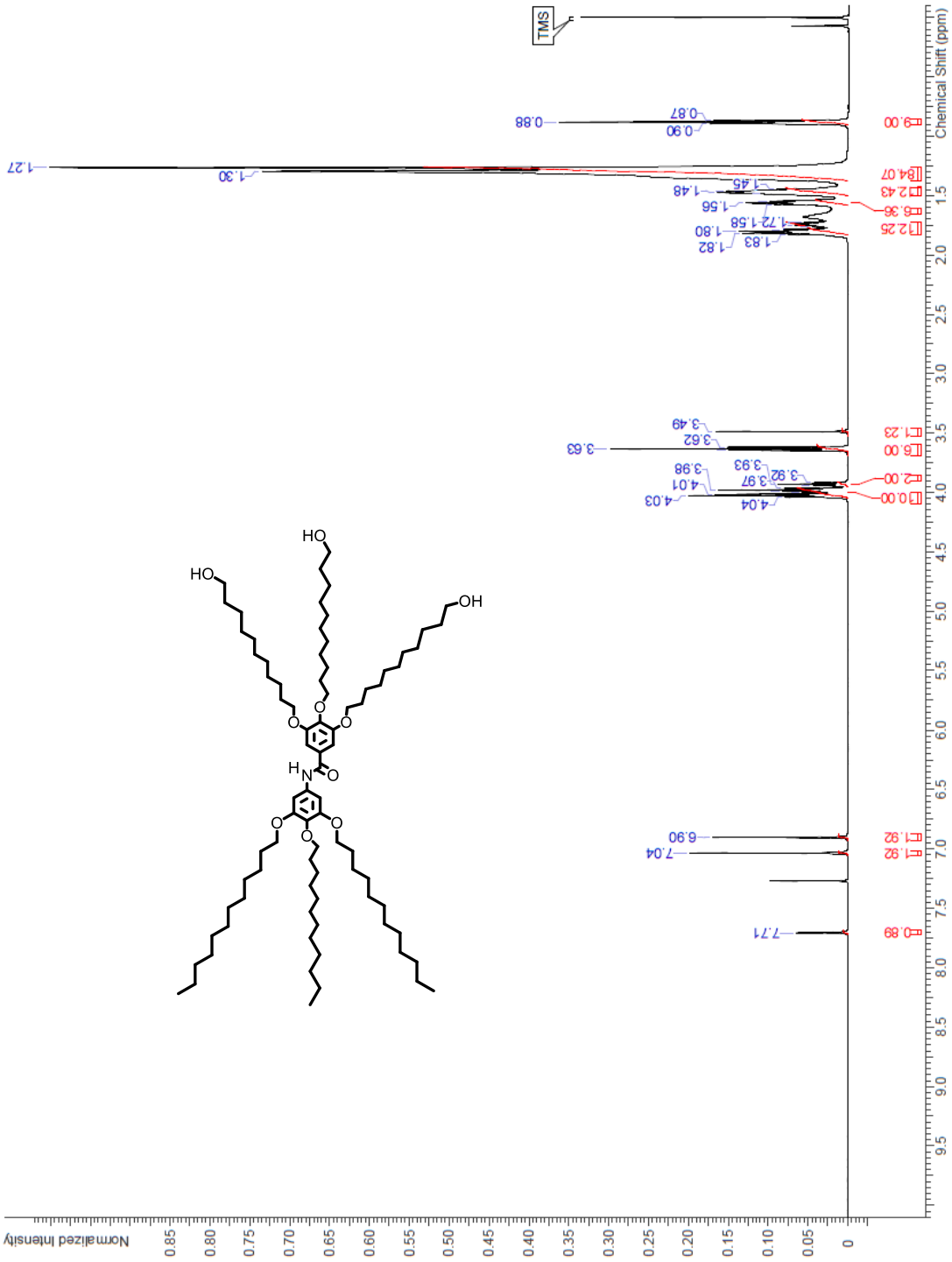

TMS
CHLOROFORM-d
14.02
22.60
26.01
29.22
29.31
31.77
31.84
69.14
69.47
73.54
99.15
105.77
129.95
133.57
135.06
141.58
153.30
165.55
Chemical Shift (ppm)
Normalized Intensity
OC8H17
C8H17O
OC8H17
O
N
H
C8H17O
OC8H17
OC8H17

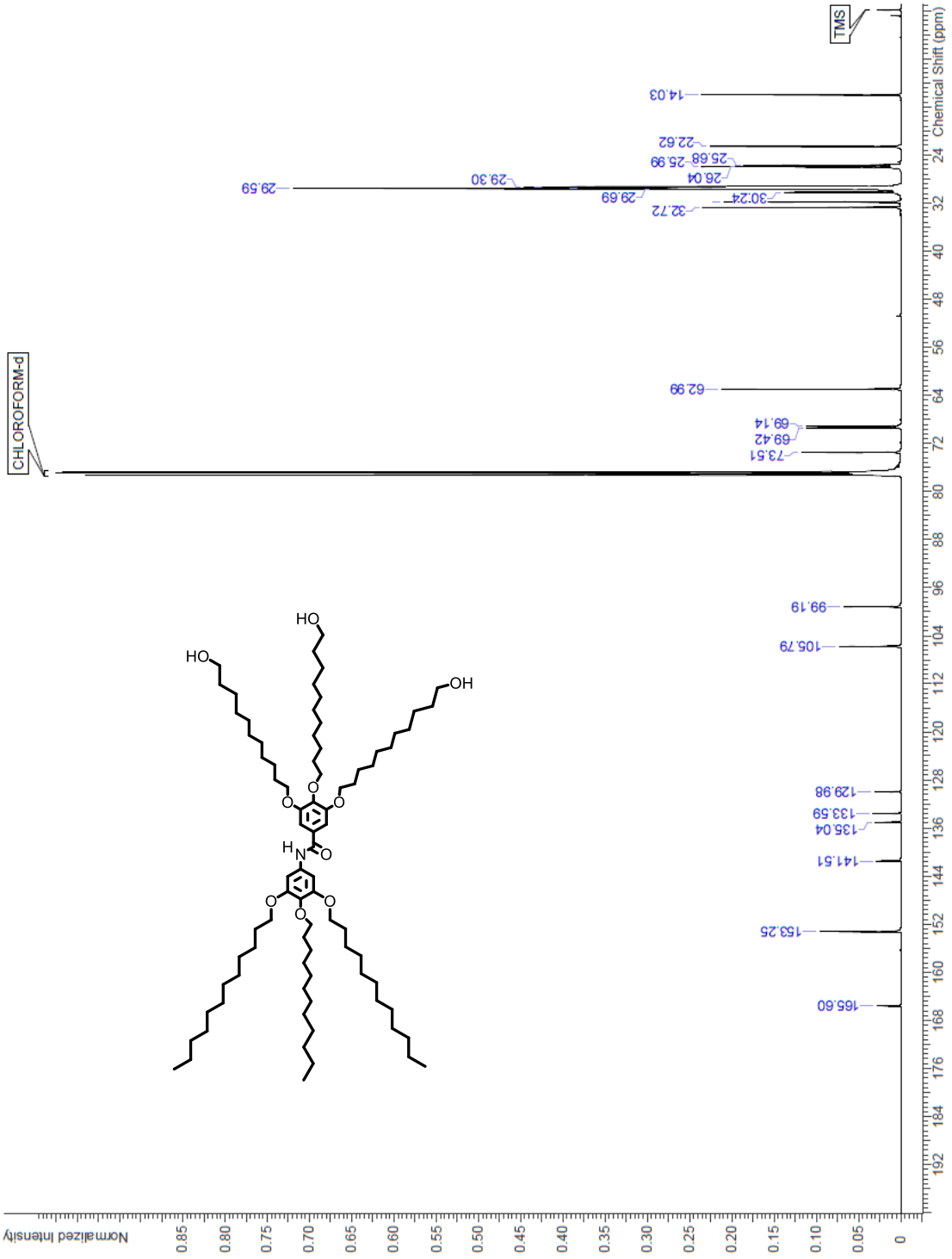

TMS
Water
CHLOROFORM-d
0.88
0.89
0.90
1.30
1.48
1.56
1.73
1.79
1.80
1.82
1.83
1.84
3.62
3.64
3.93
3.97
3.98
4.02
4.03
4.04
6.91
7.04
9.00
60.35
5.22
5.34
2.11
5.56
1.96
9.66
1.71
1.77
0.64
Chemical Shift (ppm)
Normalized Intensity
HO
OH
OH
O
O
O
O
O
O
O
O
N
H

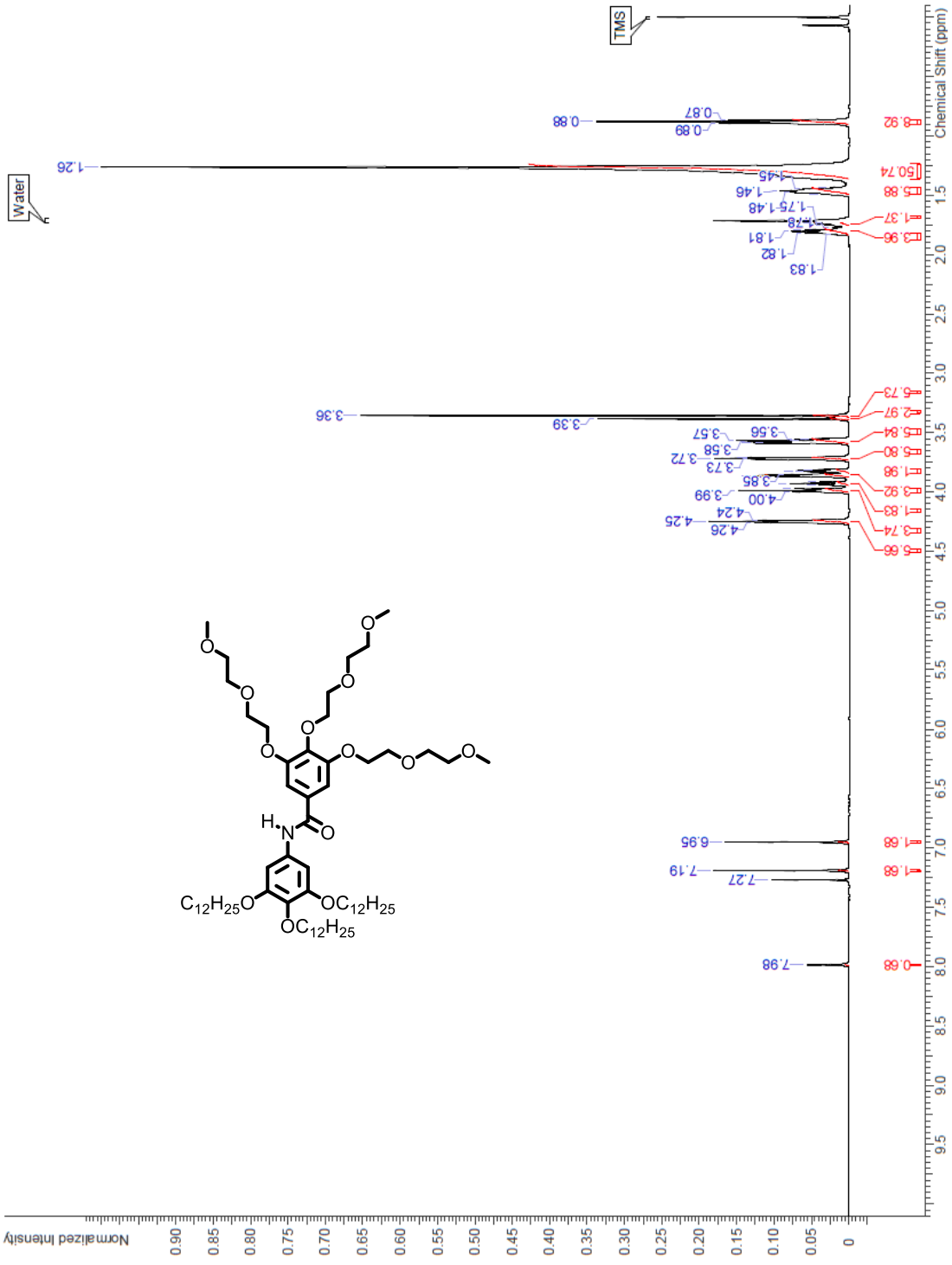

TMS
CHLOROFORM-d
14.02
22.60
25.68
25.99
26.02
29.23
29.31
29.51
31.78
32.73
63.00
69.14
69.43
73.51
99.19
105.79
129.98
133.59
135.05
141.52
153.26
165.60
OH
OH
HO
O
O
O
O
O
O
O
N
H
Chemical Shift (ppm)
Normalized Intensity

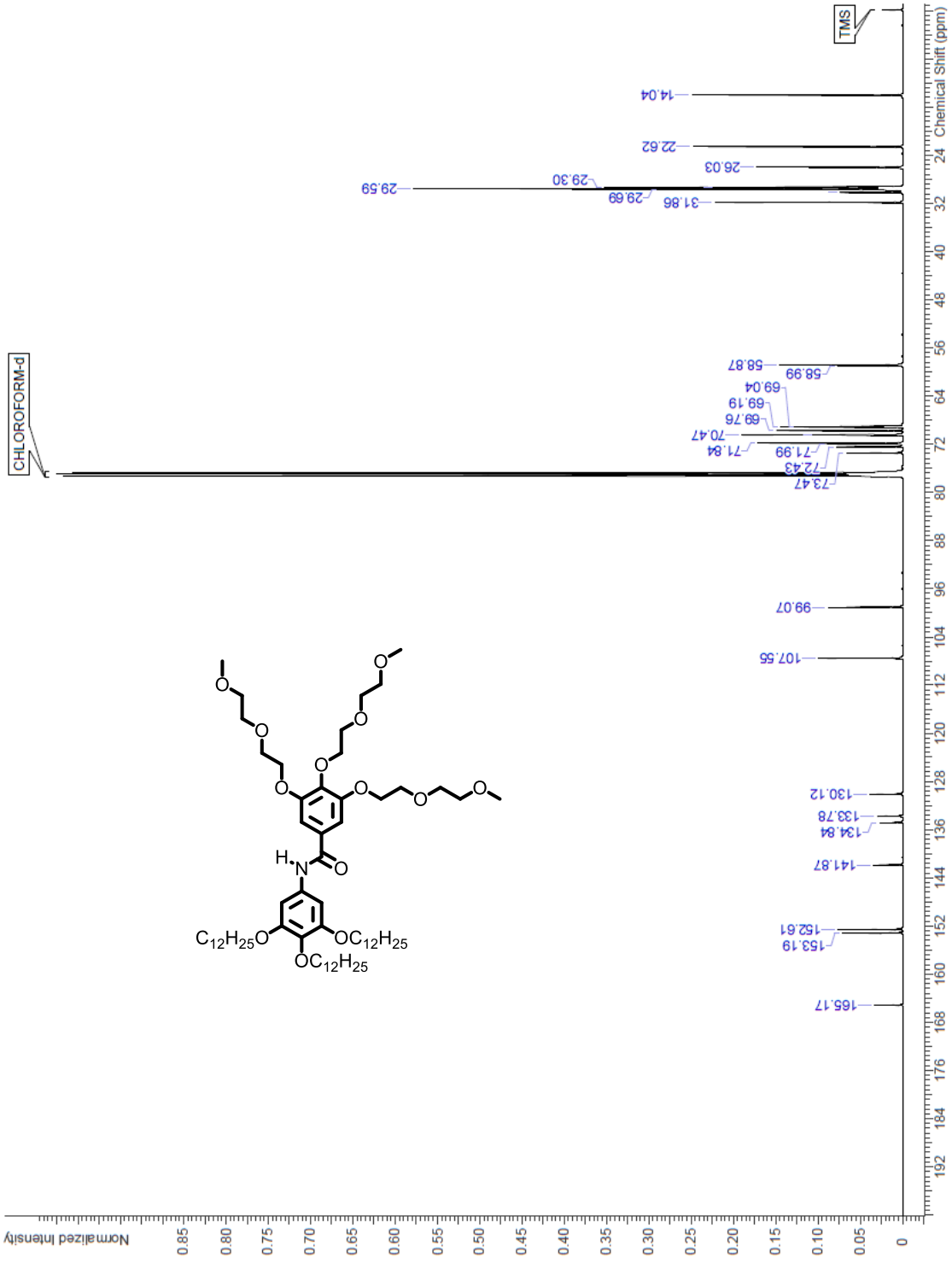

TMS
Water
0.87
0.89
0.90
1.27
1.45
1.47
1.48
1.49
1.78
1.81
1.82
1.84
1.85
3.92
3.94
3.98
3.99
4.02
4.03
4.06
6.90
7.03
7.59
Chemical Shift (ppm)
Normalized Intensity
$OC_{12}H_{25}$
$C_{12}H_{25}O$
$OC_{12}H_{25}$
H
N
O
$C_{12}H_{25}O$
$OC_{12}H_{25}$
$OC_{12}H_{25}$

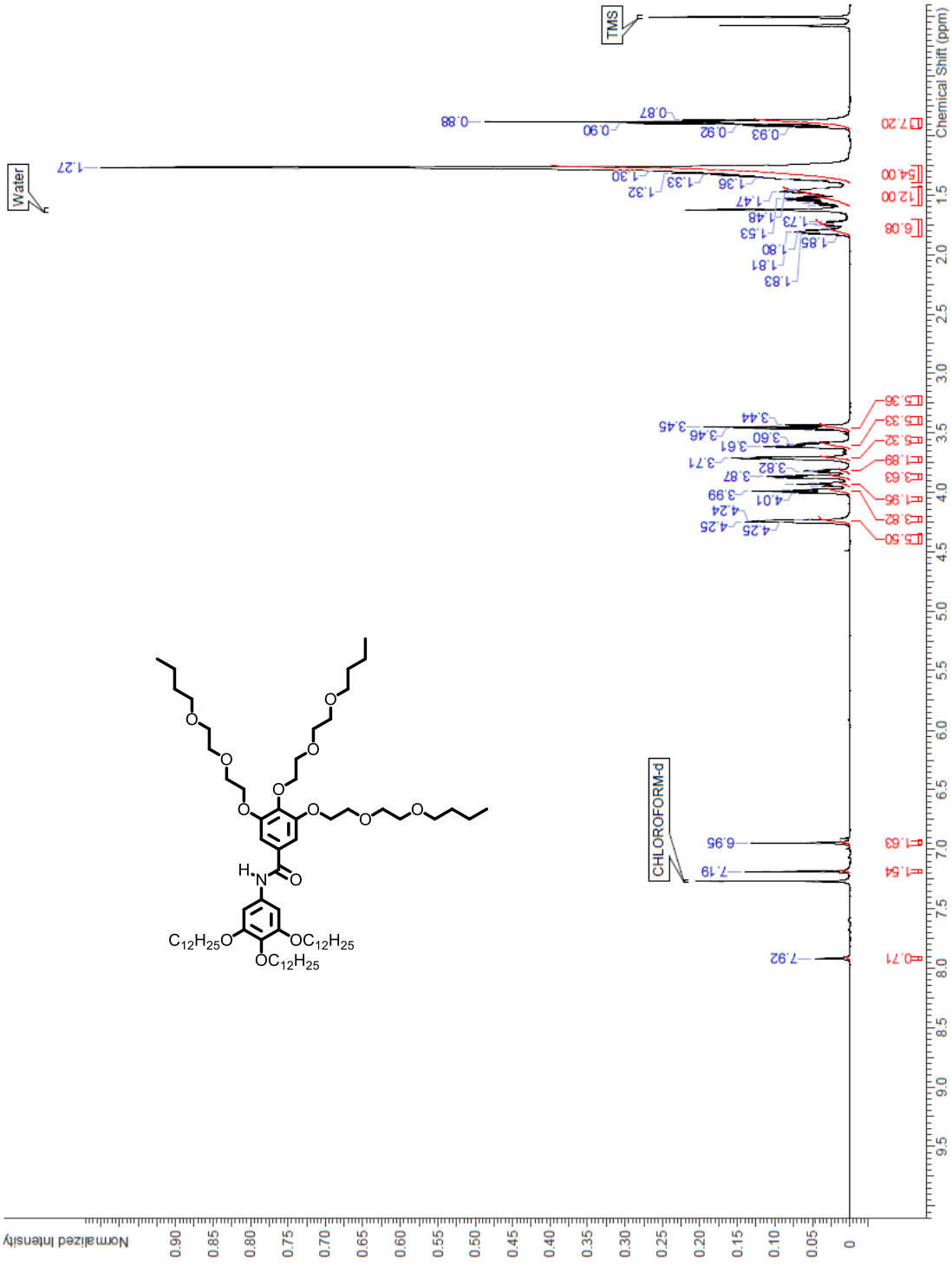

TMS
CHLOROFORM-d
14.05
22.63
26.03
29.32
29.60
31.88
69.16
69.49
73.55
99.15
105.78
129.96
133.56
135.08
141.60
153.31
165.54
Chemical Shift (ppm)
Normalized Intensity
OC12H25
C12H25O
OC12H25
H
N
O
C12H25O
OC12H25
OC12H25

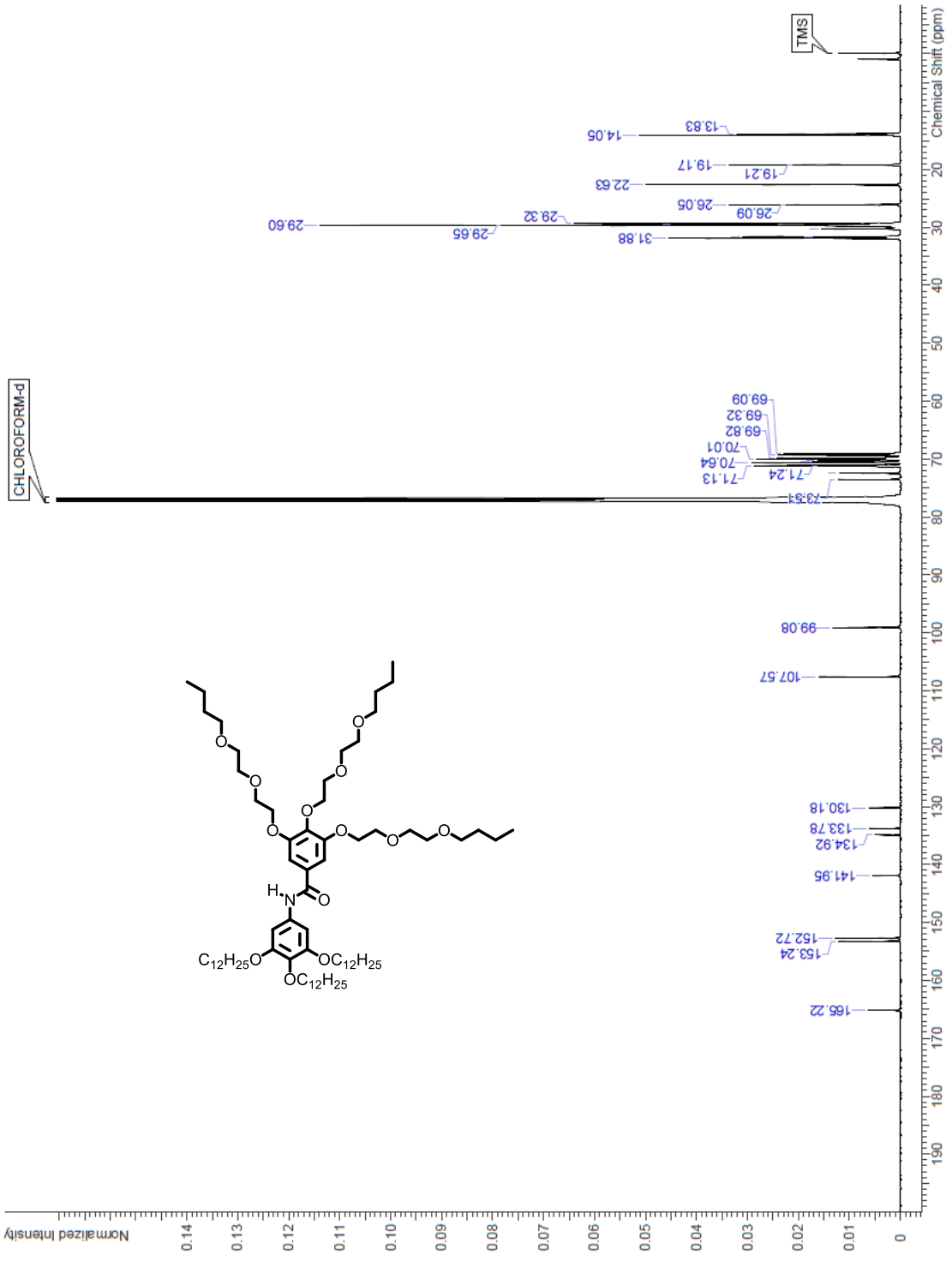

TMS
0.88
0.87
0.90
1.27
1.30
1.45
1.48
1.56
1.72-1.58
1.80
1.82
1.83
3.49
3.62
3.63
3.92
3.97
3.93
3.98
4.01
4.03
4.04
6.90
7.04
7.71
9.00
84.07
12.43
56.36
12.25
1.23
6.00
2.00
10.00
1.92
1.92
0.89
Chemical Shift (ppm)
Normalized Intensity
HO
HO
OH
O
O
O
O
O
O
O
O
H
N
O

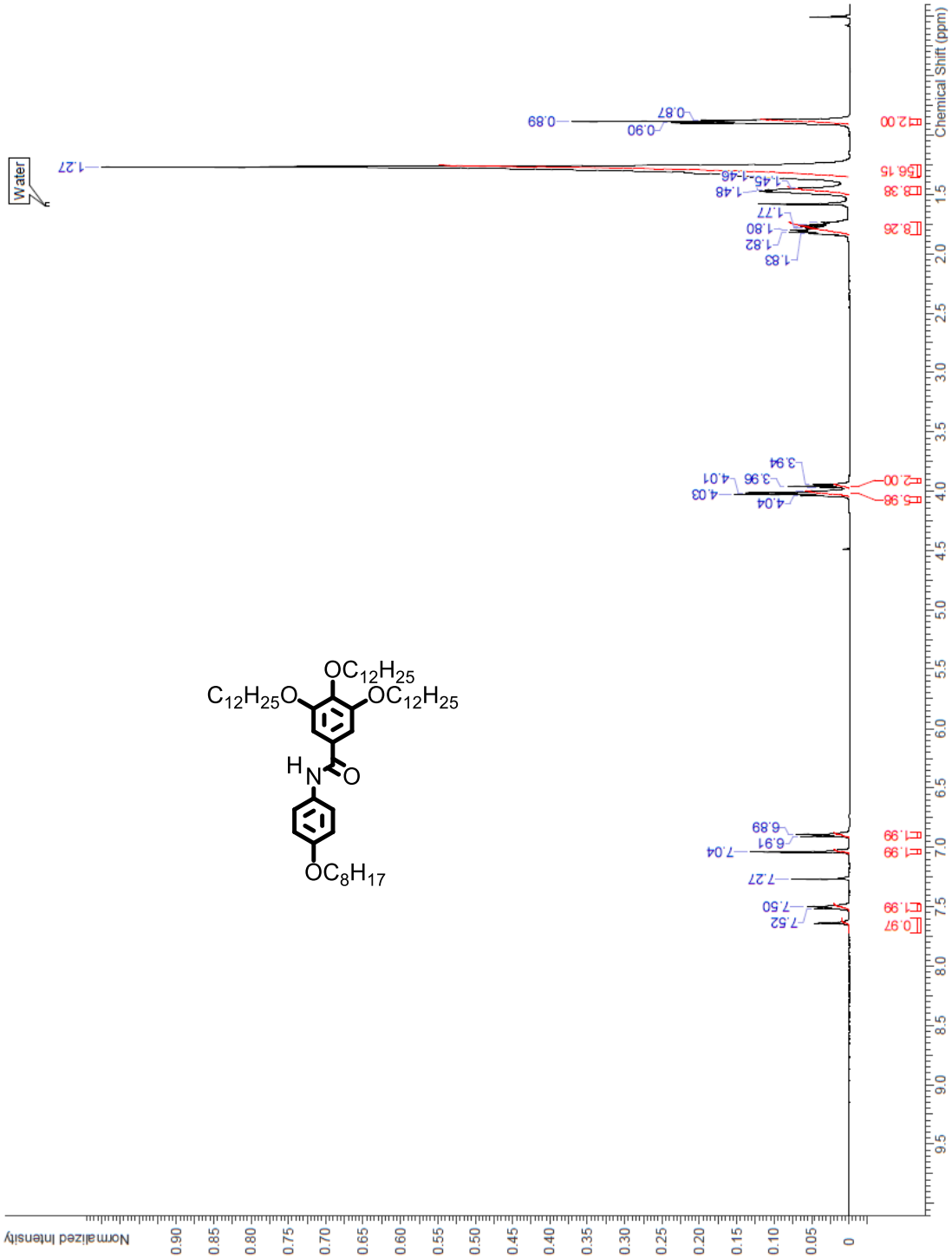

TMS
CHLOROFORM-d
14.03
22.62
25.68
25.99
26.04
29.30
29.59
29.69
30.24
32.72
62.99
69.14
69.42
73.51
99.19
105.79
129.98
133.59
135.04
141.51
153.25
165.60
HO
HO
OH
O
O
O
O
O
O
O
H
N
O
Chemical Shift (ppm)
Normalized Intensity

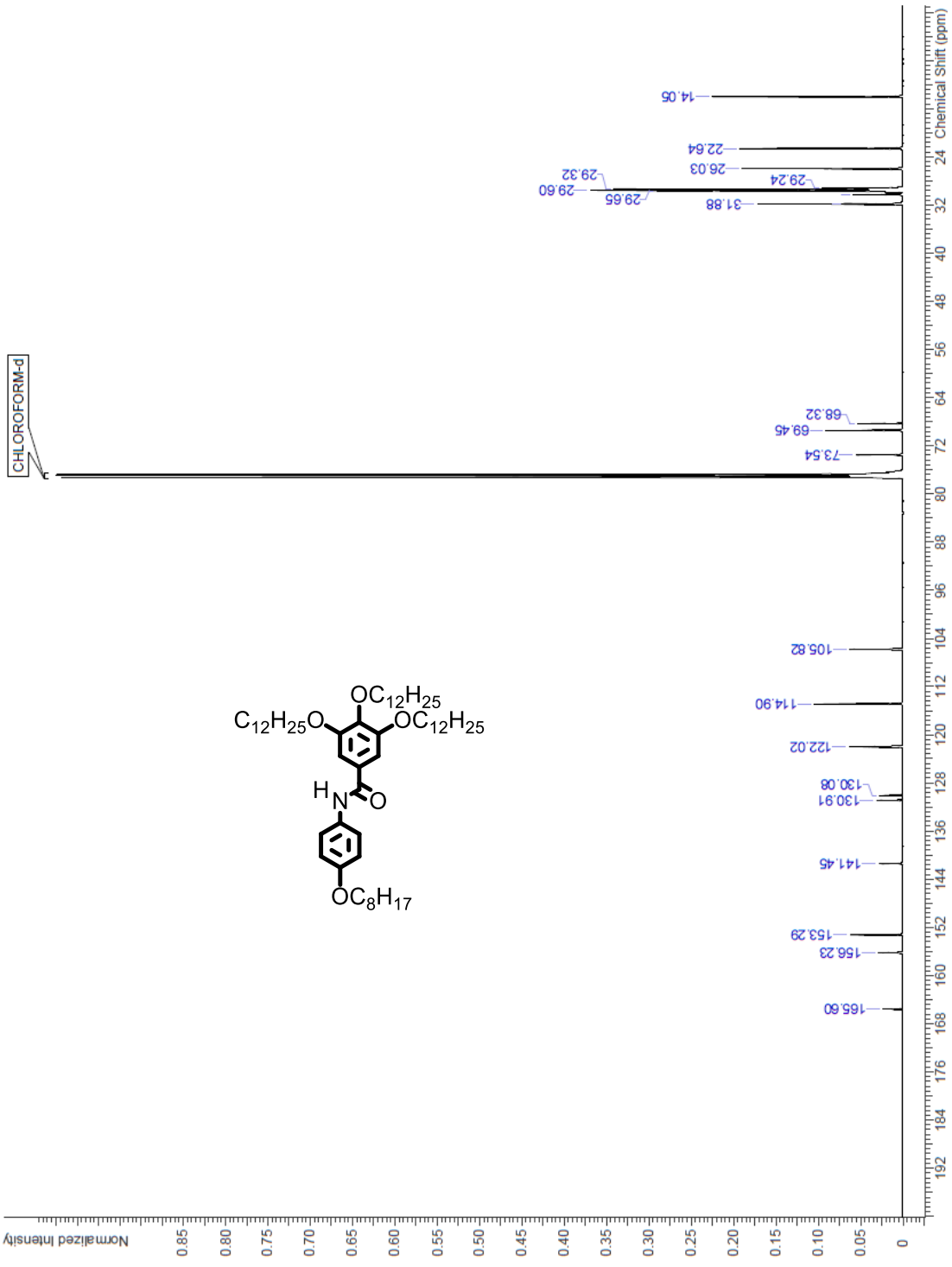

TMS
Water
0.87
0.88
0.89
1.26
1.45
1.46
1.75-1.48
1.81
1.82
1.83
3.36
3.39
3.56
3.57
3.58
3.72
3.73
3.85
3.99
4.00
4.24
4.25
4.26
6.95
7.19
7.27
7.98
8.92
50.74
5.88
1.37
3.96
5.73
2.97
5.84
5.80
1.98
3.92
1.83
3.74
5.66
1.68
1.68
0.68
Chemical Shift (ppm)
Normalized Intensity
$C_{12}H_{25}O$
$OC_{12}H_{25}$
$OC_{12}H_{25}$

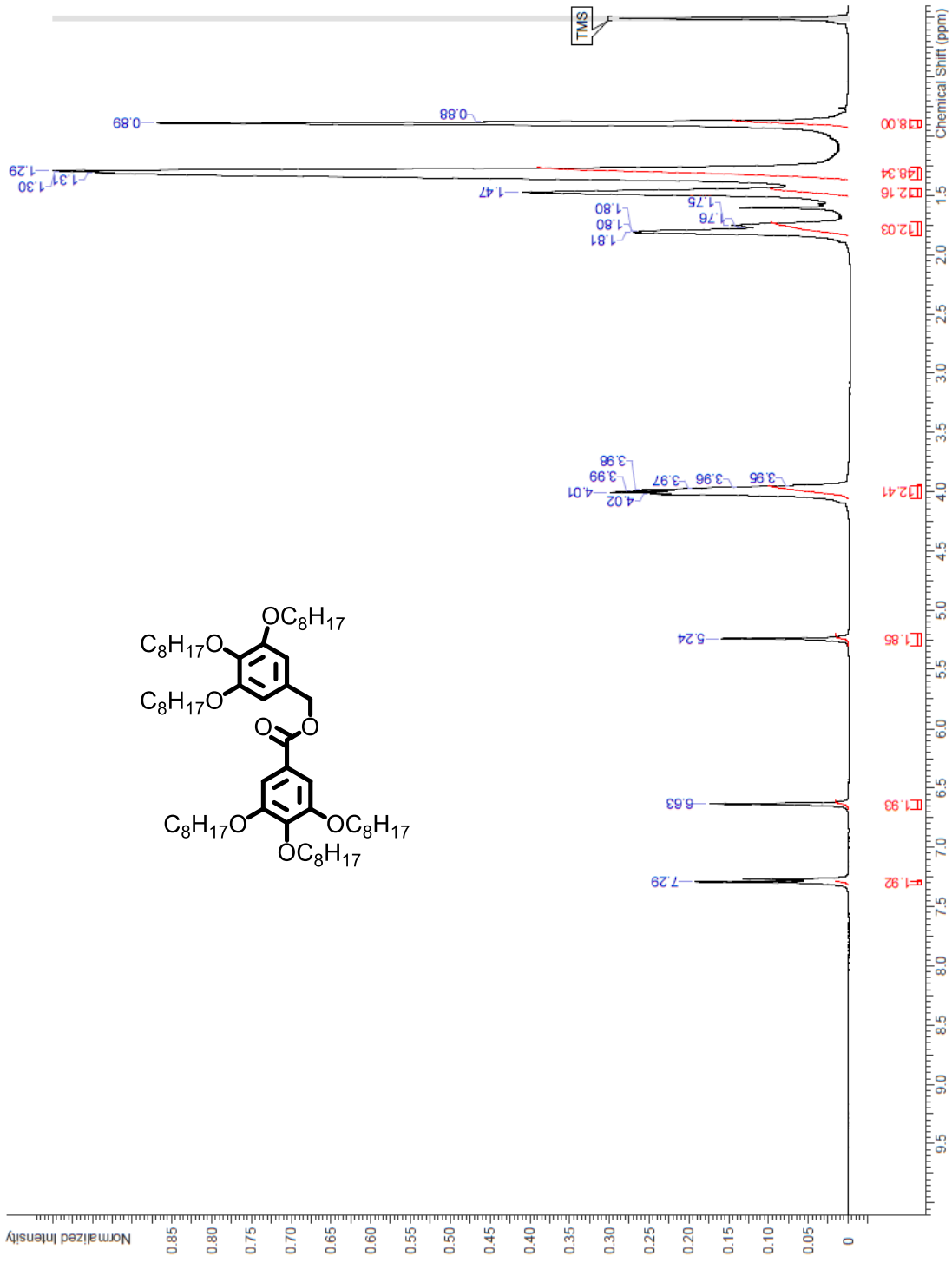

TMS
CHLOROFORM-d
14.04
22.62
26.03
29.30
29.59
29.69
31.86
58.87
58.99
69.04
69.19
69.76
70.47
71.84
71.99
72.43
73.47
99.07
107.55
130.12
133.78
134.84
141.87
152.61
153.19
165.17
Chemical Shift (ppm)
Normalized Intensity
$C_{12}H_{25}O$
$OC_{12}H_{25}$
$OC_{12}H_{25}$

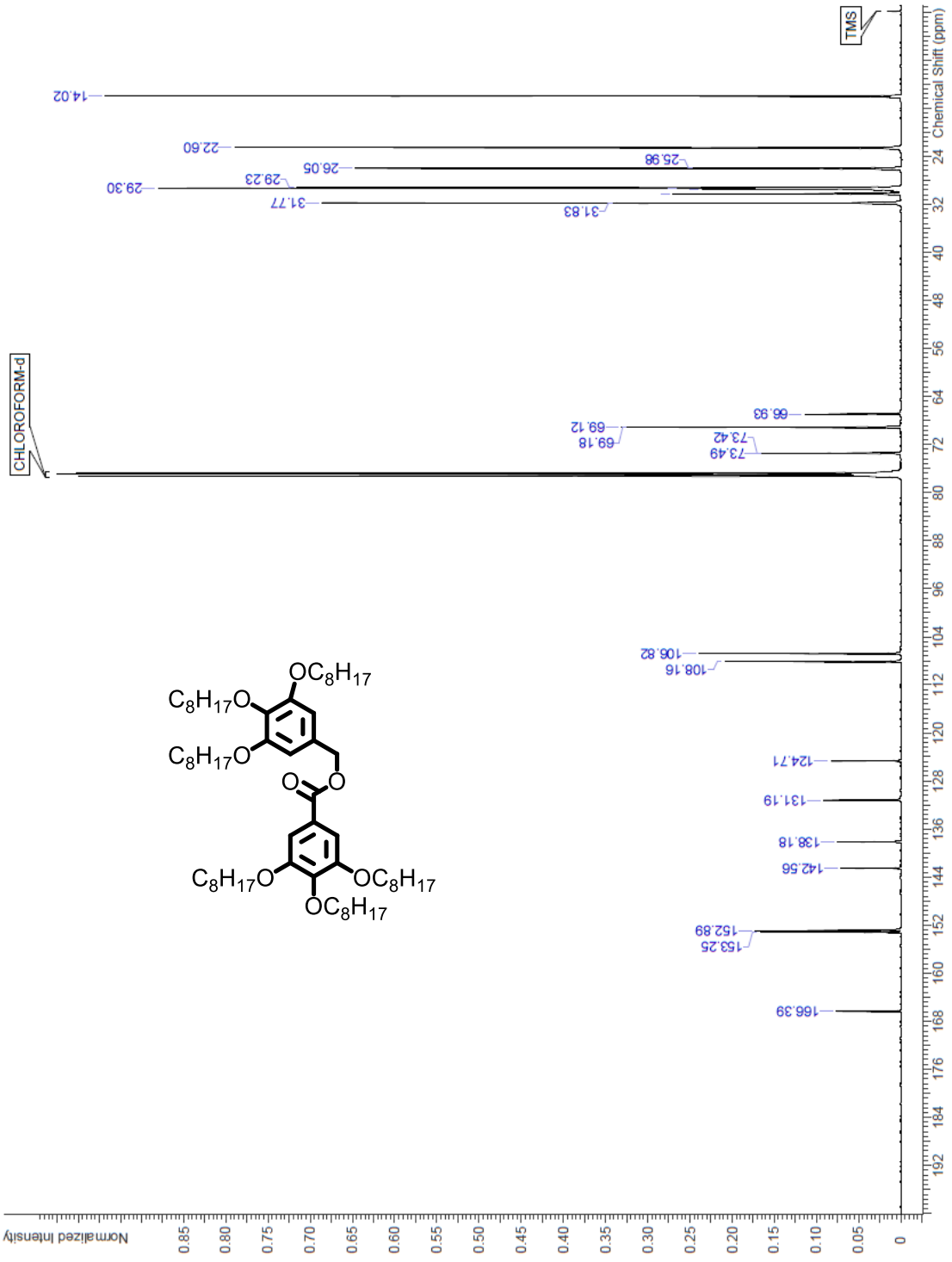

TMS
Water
CHLOROFORM-d
Chemical Shift (ppm)
Normalized Intensity
H
N
O
$C_{12}H_{25}O$
$OC_{12}H_{25}$
$OC_{12}H_{25}$

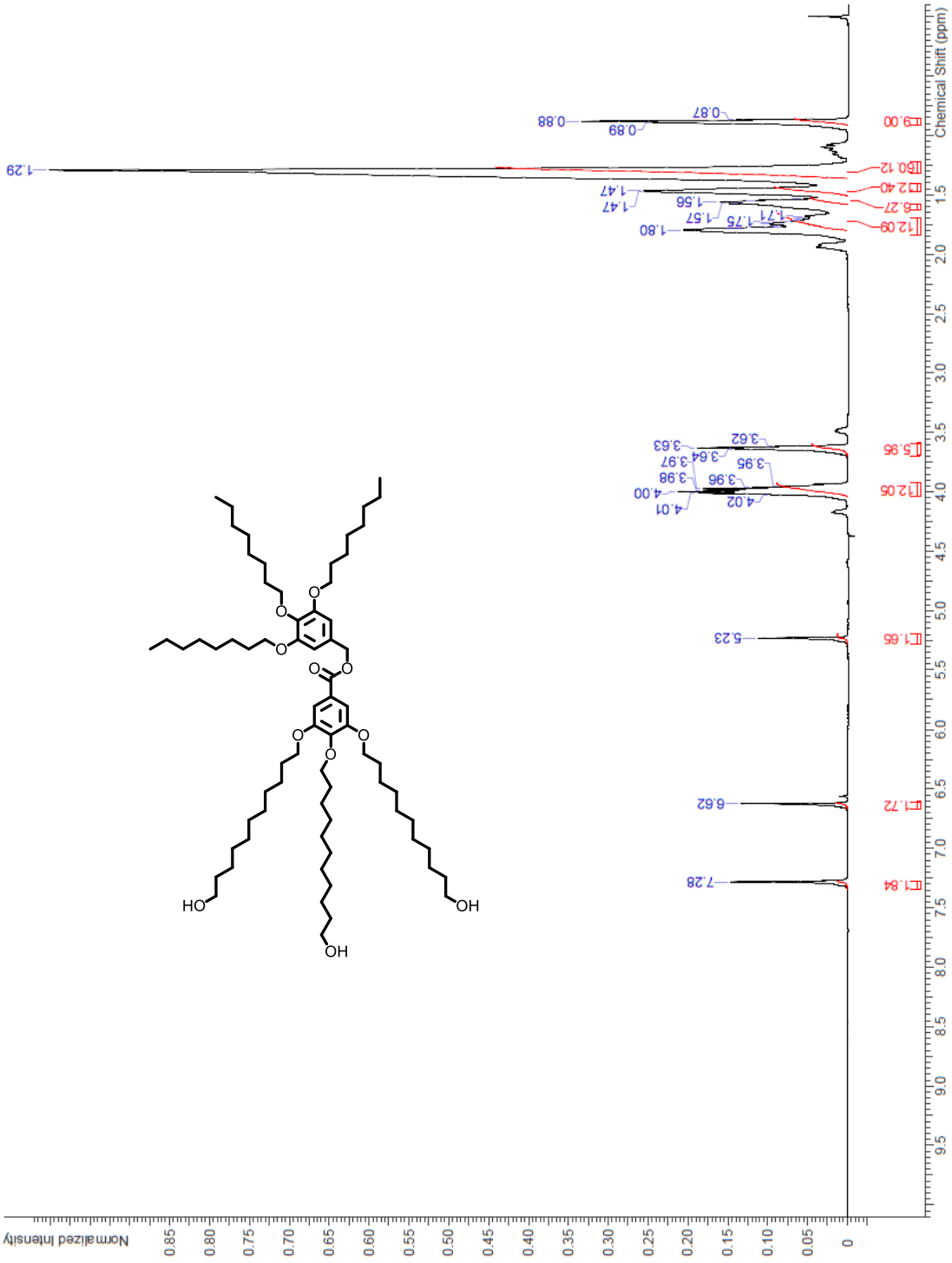

TMS
CHLOROFORM-d
13.83
14.05
19.17
19.21
22.63
26.05
26.09
29.32
29.60
29.65
31.88
69.09
69.32
69.82
70.01
70.64
71.13
71.24
73.51
99.08
107.57
130.18
133.78
134.92
141.95
152.72
153.24
165.22
Chemical Shift (ppm)
Normalized Intensity
$C_{12}H_{25}O$
$OC_{12}H_{25}$
$OC_{12}H_{25}$

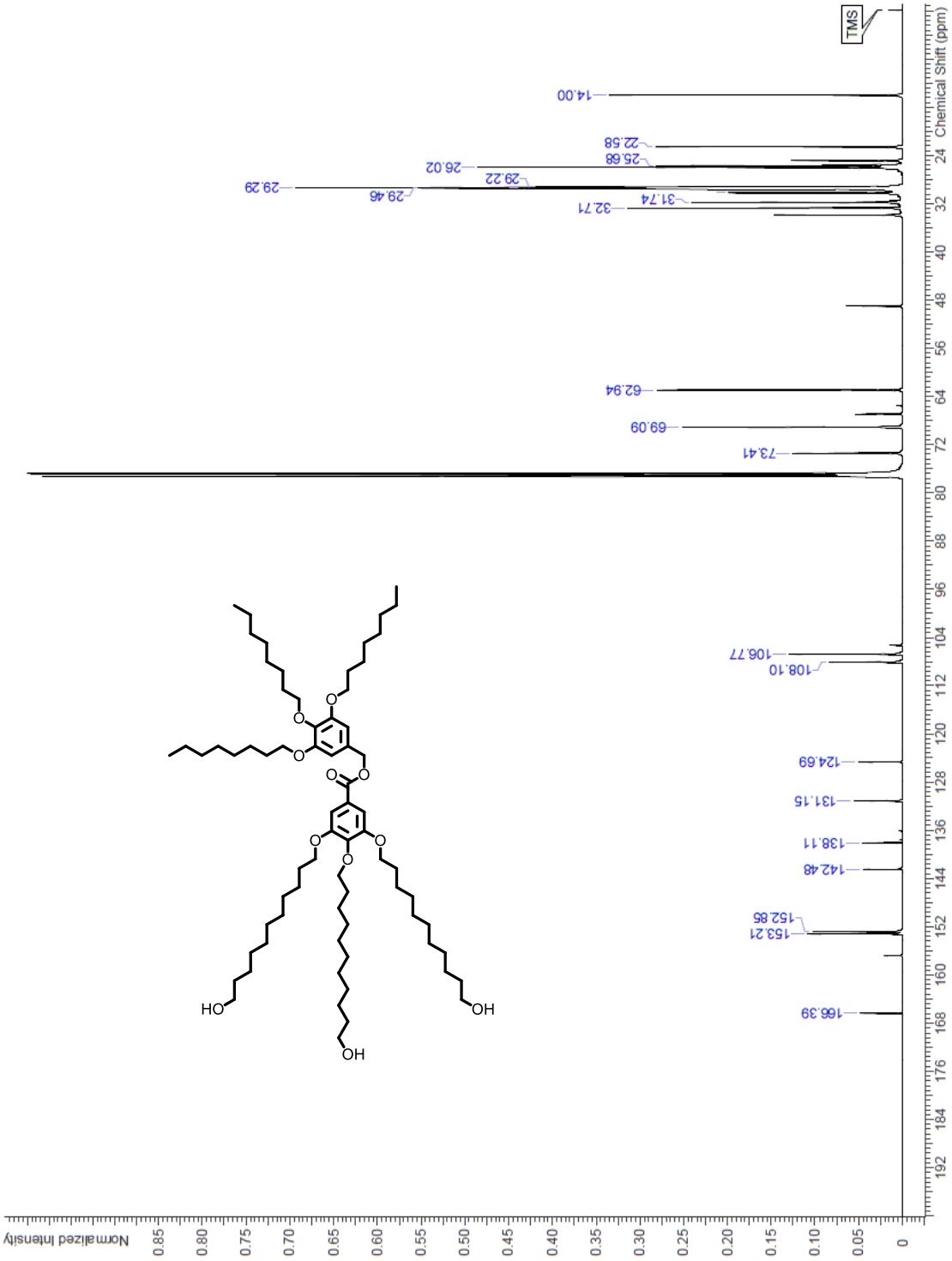

Water
1.27
0.87
0.89
0.90
1.45
1.46
1.48
1.77
1.80
1.82
1.83
3.94
3.96
4.01
4.03
4.04
6.89
6.91
7.04
7.27
7.50
7.52
2.00
56.15
8.38
8.26
2.00
5.98
1.99
1.99
1.99
0.97
Chemical Shift (ppm)
Normalized Intensity
OC12H25
C12H25O
OC12H25
H
N
O
OC8H17

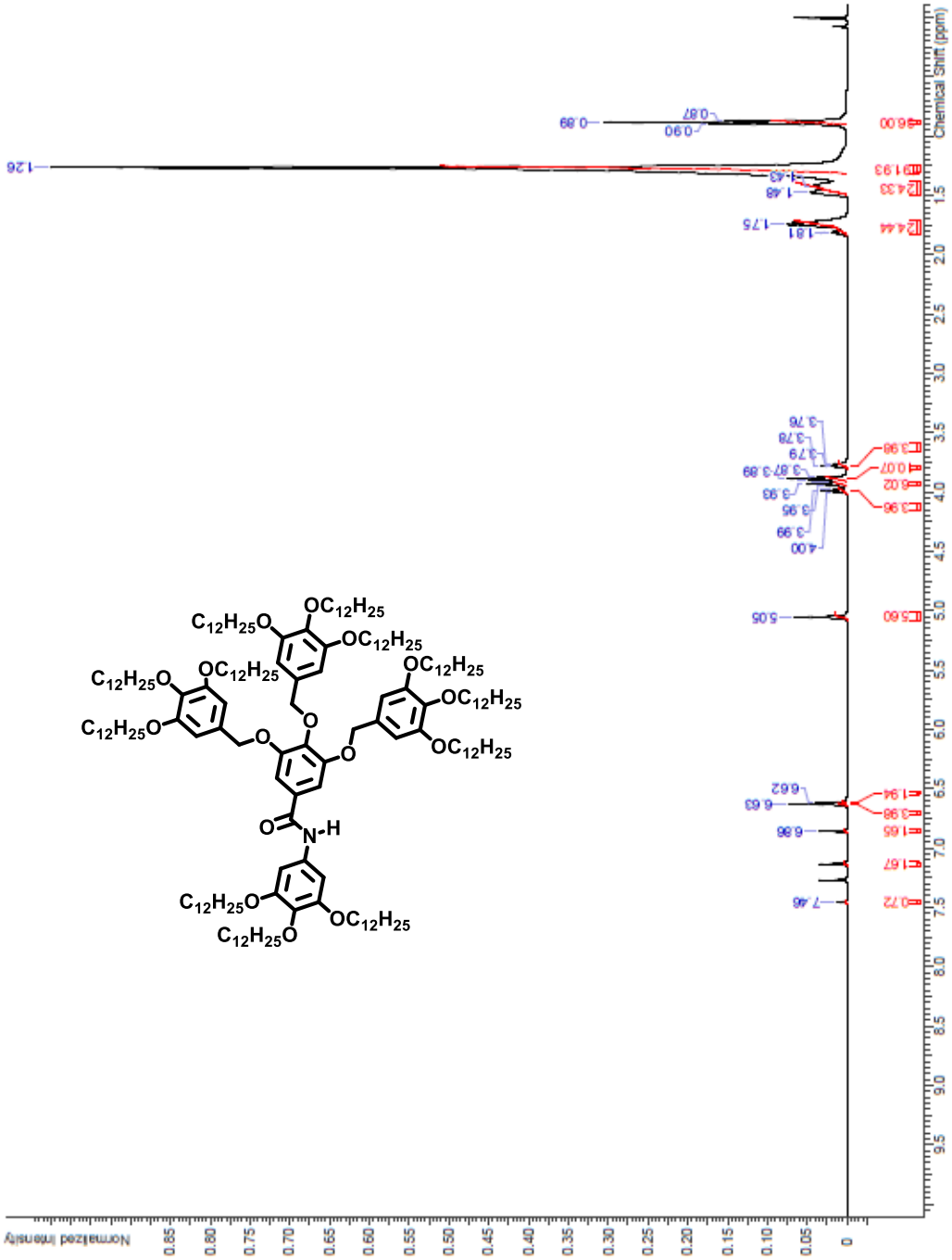

CHLOROFORM-d
14.05
22.64
26.03
29.24
29.32
29.60
29.65
31.88
68.32
69.45
73.54
105.82
114.90
122.02
130.08
130.91
141.45
153.29
156.23
165.60
Chemical Shift (ppm)
Normalized Intensity

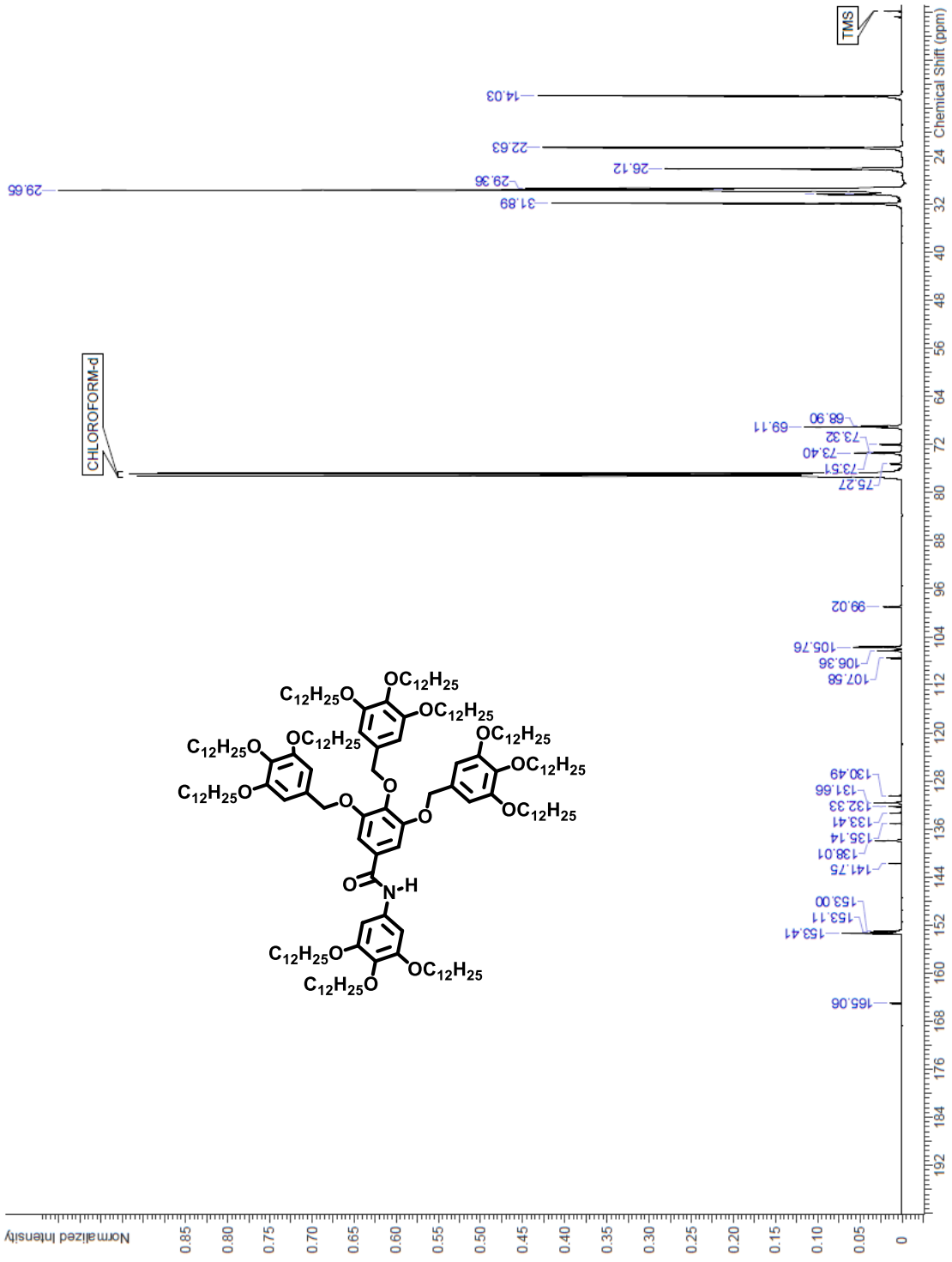

TMS
0.89
0.88
1.29
1.30
1.31
1.47
1.75
1.76
1.80
1.80
1.81
3.96
3.96
3.97
3.98
3.99
4.01
4.02
5.24
6.63
7.29
8.00
8.34
2.16
2.03
2.41
1.85
1.93
1.92
Chemical Shift (ppm)
Normalized Intensity
$C_8H_{17}O$
$C_8H_{17}O$
OC_8H_{17}
O
O
$C_8H_{17}O$
OC_8H_{17}
OC_8H_{17}

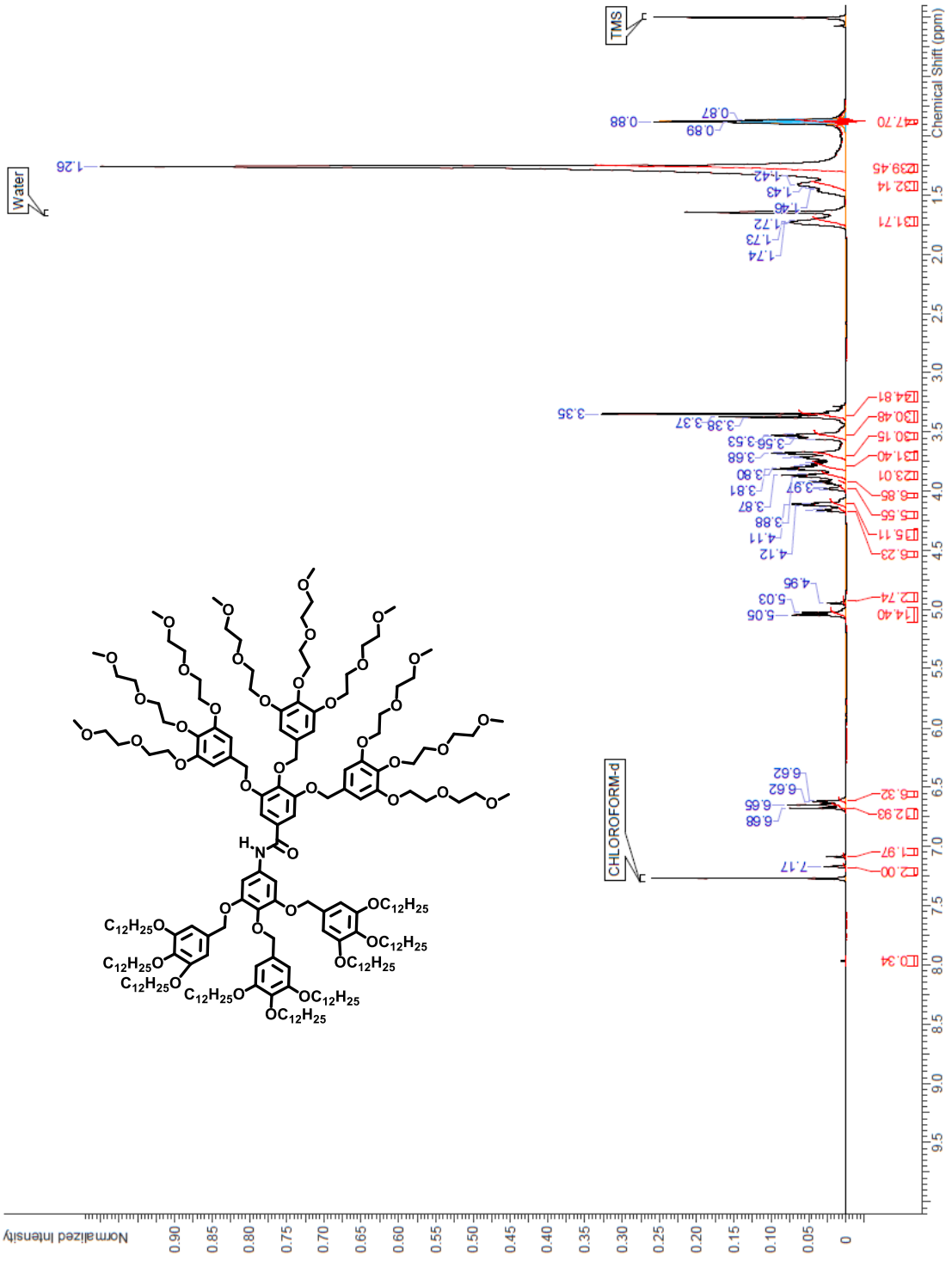

TMS
CHLOROFORM-d
14.02
22.60
25.98
26.05
29.23
29.30
31.77
31.83
66.93
69.12
69.18
73.42
73.49
106.82
108.16
124.71
131.19
138.18
142.56
152.89
153.25
166.39
Chemical Shift (ppm)
Normalized Intensity
OC8H17
C8H17O
C8H17O
O
O
C8H17O
OC8H17
OC8H17

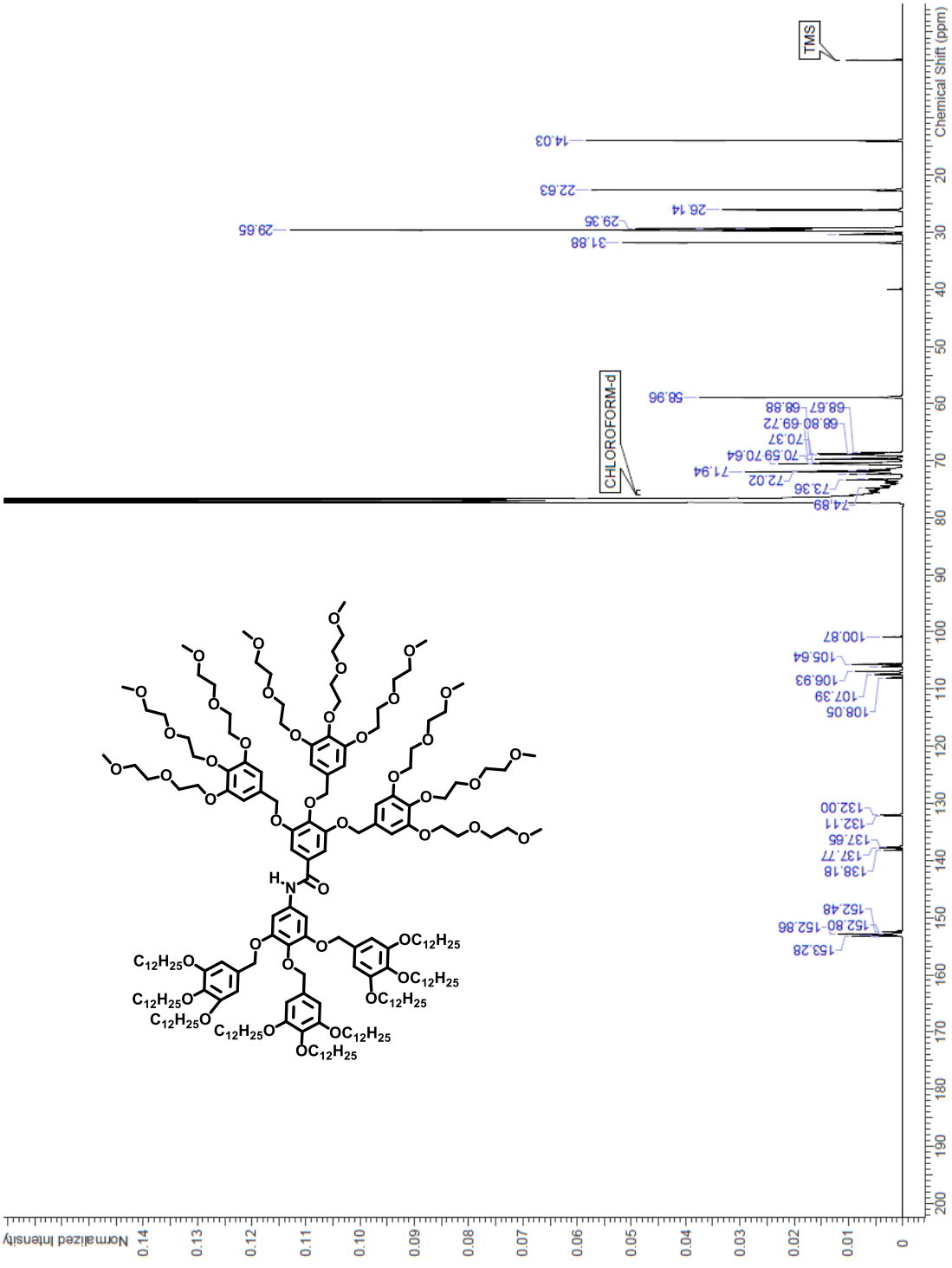

Chemical Shift (ppm)
Normalized Intensity
HO
OH
OH
OH


TMS
14.00
22.58
25.68
26.02
29.22
29.46
29.29
31.74
32.71
62.94
69.09
73.41
106.77
108.10
124.69
131.15
138.11
142.48
152.85
153.21
166.39
HO
OH
OH
Chemical Shift (ppm)
Normalized Intensity


Chemical Shift (ppm)
Normalized Intensity
0.89
0.87
0.90
1.26
1.43
1.48
1.75
1.81
3.76
3.78
3.79
3.87
3.89
3.93
3.95
3.99
4.00
5.05
6.62
6.63
6.86
7.46
46.00
19.93
24.33
24.44
3.98
0.07
6.02
3.98
5.60
1.94
3.98
1.65
1.67
0.72
N-H


TMS
CHLOROFORM-d
14.03
22.63
26.12
29.36
29.65
31.89
68.90
69.11
73.32
73.40
73.51
75.27
99.02
105.76
106.36
107.58
130.49
131.66
132.33
133.41
135.14
138.01
141.75
153.00
153.11
153.41
165.06
Chemical Shift (ppm)
Normalized Intensity
$C_{12}H_{25}O$
$OC_{12}H_{25}$
O
N-H


TMS
Water
CHLOROFORM-d
Chemical Shift (ppm)
Normalized Intensity
0.87
0.88
0.89
1.26
1.42
1.43
1.46
1.72
1.73
1.74
3.35
3.37
3.38
3.53
3.55
3.68
3.80
3.81
3.87
3.88
3.97
4.11
4.12
4.95
5.03
5.05
6.62
6.62
6.65
6.68
7.17
$C_{12}H_{25}O$
$OC_{12}H_{25}$


TMS
CHLOROFORM-d
14.03
22.63
26.14
29.35
29.65
31.88
58.96
68.67
68.88
68.80
69.72
70.37
70.59
70.64
71.94
72.02
73.36
74.89
100.87
105.64
106.93
107.39
108.05
132.00
132.11
137.65
137.77
138.18
152.48
152.80
152.86
153.28
Chemical Shift (ppm)
Normalized Intensity
H
N
O
$C_{12}H_{25}O$
$OC_{12}H_{25}$

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